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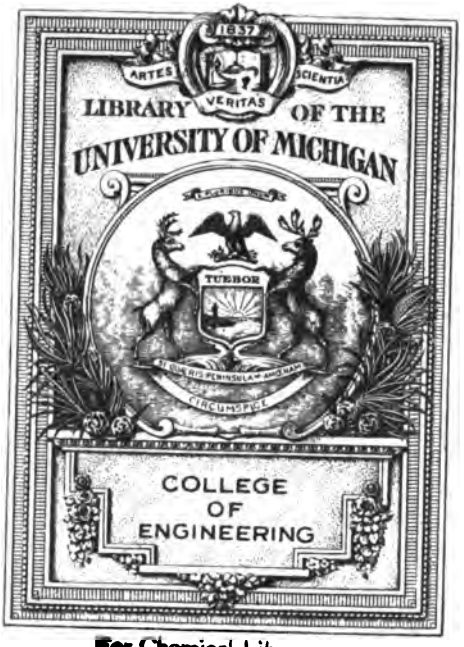

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CONCENTRATION BY FLOTATION

Compiled and Edited

BY

T. A. RICKARD

Associate of the Royal School of Mines, Member of the American Institute of Mining and Metallurgical Engineers, and of the Institution of Mining and Metallurgy. Author of "The Flotation Process," "Technical Writing," and "Journeys of Observation"

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PREFACE

THIS BOOK is a compilation of articles appearing in the *Mining and Scientific Press* during the years 1915 to 1920. Five of the articles were reprinted in a book entitled "The Flotation Process," by T. A. Rickard, published in 1916, and seventeen of them appeared in "Flotation," by T. A. Rickard and O. C. Ralston, published in 1917. Only small editions of these books were printed and the supply of both was speedily exhausted. Since then no book on the subject has been provided to fill the current need of those engaged in the use and development of the flotation process. Hence this volume, which, besides the twenty-two articles already mentioned, contains eighteen later articles on the subject, and thus serves as a convenient compendium of the principal literature on the technology of the process. As editor of the *Mining and Scientific Press*, I am responsible for the editing and selection of the material it contains. It does not pretend to be complete or final; no book that could be considered a comprehensive treatise can be written on the theory and technique of a metallurgical process that is still so imperfectly understood and that continues to undergo such radical changes. It is my hope that the information given in this compilation of technical writings will be helpful to those engaged in the concentration of ores by flotation. If this hope be fulfilled, the book will have justified its existence.

T. A. RICKARD.

SAN FRANCISCO,
December 1, 1920.

CONTENTS

		PAGE
PREFACE		iii
A GLOSSARY OF FLOTATION	*By T. A. Rickard*	vii
THE HISTORY OF FLOTATION	*By T. A. Rickard*	1
PRINCIPLES OF FLOTATION	*By T. A. Rickard*	32
THE FLOTATION OF GOLD AND SILVER MINERAL	*By T. A. Rickard*	78
FLOTATION LITIGATION. I	*By T. A. Rickard*	100
FLOTATION LITIGATION. II	*By T. A. Rickard*	120
TESTING ORES FOR THE FLOTATION PROCESS,	*By O. C. Ralston and Glenn L. Allen*	137
TESTING ORES FOR FLOTATION	*By James M. Hyde*	166
FLOTATION IN A MEXICAN MILL	*By R. T. Mishler*	182
FLOTATION AT THE CENTRAL MINE, BROKEN HILL	*By James Hebbard*	196
CYANIDE TREATMENT OF FLOTATION CONCENTRATE,	*By Charles Butters and J. E. Clennell*	214
DISPOSAL OF FLOTATION RESIDUE	*By W. Shellshear*	237
FLOTATION PRINCIPLES	*By C. Terry Durell*	248
THE THEORY OF FLOTATION	*By H. Hardy Smith*	267
THE FLOTATION OF MINERALS	*By Robert J. Anderson*	277
PRINCIPLES UNDERLYING FLOTATION	*By Joel H. Hildebrand*	291
MOLECULAR FORCES AND FLOTATION	*By Will H. Coghill*	300
THE ARMOR IN FLOTATION	*By Will H. Coghill*	325
THEORY OF ORE FLOTATION	*By H. P. Corliss and C. L. Perkins*	334
COLLOIDS	*By E. E. Free*	354
DIFFERENTIAL FLOTATION	*By O. C. Ralston*	378
FLOTATION AT THE CALAVERAS COPPER	*By Hallet R. Robbins*	402
THE DISPOSAL OF FLOTATION PRODUCTS	*By Robert S. Lewis*	415
MECHANICAL DEVELOPMENT IN FLOTATION	*By O. C. Ralston*	442
THE FLOTATION OF OXIDIZED ORES	*By Glenn L. Allen and Oliver C. Ralston*	486
FLOTATION AT COBALT, ONTARIO	*By W. E. Simpson*	509
CASCADE METHOD OF FROTH-FLOTATION	*By H. Hardy Smith*	524
FLOTATION OF SEMI-OXIDIZED SILVER ORE	*By E. J. Atkison*	536
THE DEVELOPMENT OF FLOTATION AT THE BROKEN HILL PROPRIETARY MINE, AUSTRALIA	*By Edwin T. Henderson*	545
THE BRADFORD PROCESS AT BROKEN HILL	*By Edwin T. Henderson*	559
THE FLOTATION OF GALENA AT THE CENTRAL MINE, BROKEN HILL,	*By R. J. Harvey*	569
RECOVERY OF COPPER FROM FLOTATION BY LEACHING	*By Percy R. Middleton*	586
THE HORWOOD PROCESS AS APPLIED TO THE COPPER-ZINC ORE OF THE AFTERTHOUGHT MINE	*By A. H. Heller*	592

PAGE

A Modification of Horwood's Process for the Treatment of Copper-Zinc Ores.....*By H. L. Hazen* 610
Flotation Practice of the Utah Copper Company.....*By T. A. Rickard* 615
The Smelting of Flotation Concentrate at Garfield..*By T. A. Rickard* 626
Preferential Flotation.....*By W. Shellshear* 641
Froth-Flotation at Broken Hill.....*By C. C. Freeman* 654
A Résumé of Literature on the Theory of Flotation, with Critical Notes.....*By H. R. Adam* 670

A GLOSSARY OF FLOTATION

ABSORB.—To drink in, to suck up, as a liquid by a solid, like a sponge or fuller's earth.

ADSORB.—To condense and hold a gas on the surface of a solid, particularly metals. Also the holding of a mineral particle within a liquid interface. From L. *ad*, to, and *sorbeo*, suck in.

ADHESION.—A molecular force by which bodies of matter are caused to stick together.

AGITATION is the act or state of being shaken, stirred, or moved with violence. From L. *agitatus*, *agito*, the frequentative of *ago*, to drive.

BAFFLE.—That which defeats or frustrates, hence the projections or wings that divert or interrupt the flow of pulp in a vessel.

BUBBLE.—A globule of air or other gas in a liquid; also a vesicle of water or other liquid inflated with air or other gas.

BUOY.—To keep from sinking, to keep afloat in a liquid.

COAGULATION.—The state of a solute in a solvent, or of a colloidal gel, resulting from clotting or curdling; the act of changing to a curd-like condition.

COAL-TAR is a thick, black, viscid, and opaque liquid condensed when gas is distilled from coal. This product consists of soluble and insoluble substances.

COHESION.—That force by which molecules of the same kind or of the same body are held together, so that the body resists being pulled to pieces.

COLLOID.—A state of matter supposed to represent a degree of sub-division into almost molecular dimensions, dispersed in a solvent. Colloidal particles possess the property of carrying electric charges, and also of failing to diffuse through a membrane, this being the original distinction between colloids and crystalloids.

CONCENTRATE.—To draw or gather together to a common centre. To reduce to a purer state by the removal of non-essential matter. From L. *con* or *cum*, with, and *centrum*, a centre.

CONTAMINATE.—To make impure by contact or admixture. A substance that performs the function, in an ore-pulp, along with oil, of promoting the emulsification or the de-emulsification of the oil, and thereby exerts an influence upon the making of froth for the flotation of minerals.

DISPERSOID.—A body that has been dispersed in a liquid.

EMULSION.—Milkification. A liquid mixture in which a fatty or resinous substance is suspended in minute particles, almost equivalent to molecular dispersion. From L. *emulgeo*, to drain out, in turn from *e*, out, and *mulgeo*, milk.

FAT is a white or yellowish substance forming the chief part of adipose tissue. It may be solid or liquid; it is insoluble in water; when treated with an alkali, the fatty acid unites with the alkaline base to make soap.

FILM.—A coating or layer, a thin membrane.

FLOCCULENT means resembling wool, therefore woolly. Coalescing and adhering in flocks. A cloud-like mass of precipitate in a solution. From L. *floccus*, a lock of wool.

FLOTATION is the act or state of floating, from the French *flottaison*, waterline, and *flotter*, to float, to waft.

FROTH.—A collection of bubbles resulting from fermentation, effervescence, or agitation.

GANGUE.—The non-metalliferous or non-valuable metalliferous minerals in the ore; veinstone or lode-filling.

GEL.—A form of matter in a colloidal state that does not dissolve but nevertheless remains suspended in a solvent from which it fails to precipitate without the intervention of heat or of an electrolyte.

GRANULATION is the state or process of being formed into grains or small particles. From L. *granum*, a grain.

GREASE.—Animal fat when soft, that is, in a semi-solid state, and oily or unctuous. From the French *graisse*.

HYDROPHILIC.—A property possessed by colloids whereby they take up water in conjunction with the molecules of the colloid in a manner analogous to a closed hydrated molecule. Hydrophilic colloids are valuable dispersing mediums for the making of emulsions.

LEVITATION.—The act of rendering light or buoyant. L. *levitas*, lightness, from *levis*, light.

METALLIC.—Of or belonging to metals, containing metals, more particularly the valuable metals that are the object of mining. From L. *metallum*, ore.

MINERAL.—Inorganic constituent of the earth's crust. As used in flotation the terms "mineral" or "metallic" refer to those valuable constituents in the ore that it is the object of the process to separate from the non-valuable constituents, or gangue.

MOLECULE.—The smallest part of a substance that can exist separately and still retain its composition and characteristic properties; the smallest combination of atoms that will form a given chemical compound. From F. *molecule*, diminutive from L. *moles*, mass.

OCCLUDE.—To shut or close in pores or other openings. From L. *ob*, before, *claudo*, close.

OLEIC ACID is the fatty acid contained in olive-oil combined with cresoline. Although called "acid," it is an oily substance and functions as oil in flotation operations; it is contained in most mixed oils and fats, from which it is obtained by saponification with an alkali. From L. *oleum*, oil.

OIL includes (1) fatty oils and acids, (2) essential oils, mostly of vegetal origin, such as eucalyptus and turpentine, (3) mineral oils, such as petroleum products, including lubricating oils.

OSMOSE.—The tendency of two liquids or gases to mix by passing through a membrane or porous wall separating them. From G. *osmos*, pushing.

PULP is powdered ore mixed with water.

SAPONIFICATION.—Conversion into soap; the process in which fatty substances form soap, by combination with an alkali. From L. *sapo* (n-), soap.

SCUM.—Impure or extraneous matter that rises or collects at the surface of liquids, as vegetation on stagnant water, or dross on a bath of molten metal.

Skin An outside layer, coat, or covering From A. S *scinn*, hide.

Solute The substance dissolved in a solution.

Surface tension is the contractile force at the surface of a liquid whereby resistance is offered to rupture.

Viscosity is the property of liquids that causes them to resist instantaneous change of shape or of the arrangements of their parts; internal friction; gumminess. From L. *viscum*, birdlime.

CONCENTRATION BY FLOTATION

THE HISTORY OF FLOTATION[1]

By T. A. RICKARD

INTRODUCTION

THE various flotation processes depend upon the successful application of a number of physical principles, of which three may be instanced as underlying the methods successively invented.

1. **Film suspension.**—This is typified by the floating of a needle on water. In the familiar experiment a small needle is greased, either intentionally or by the natural oil on the fingers; but when pains are taken to prevent contact with anything greasy, the needle will still float, if not too large and if carefully manipulated.[2] If the needle is too large it will not float, no matter how skillfully handled, because the force of gravity overcomes the force of surface-tension, which is the cause of this kind of flotation. Surface-tension is the force that causes the surface of a liquid to resist rupture. This, in turn, is due to the fact that the molecules at the surface have a greater coherence than the molecules within the body of the liquid. In consequence the surface acts as if it were an elastic film.

2. **Oil-buoyancy.**—This is a simple manifestation of gravity, whereby an oil, being lighter than water, will rise to the surface of a pulp and carry with it any mineral particles that have become immersed in it. The oil plays the part of a raft or boat. In order to effect flotation the volume of oil must be such that its smaller specific gravity will overcome the greater specific gravity

[1] From the *Mining and Scientific Press* of March 17 and 24, 1917.

[2] "The Flotation Process." See "Simple Problems in Flotation," by T. A. Rickard. Page 357.

of the burden it is to bear to the surface. Most oils have a specific gravity of about 0.9, as against the 1 of water; therefore the flotative margin is 10% only. If the specific gravity of a mineral is 5, then the volume of oil required to buoy it must weigh more than seven times as much. When an ore contains 4% of a mineral having a specific gravity of 5, then more than 576 pounds of oil will be required to raise the mineral in a ton of ore to the surface of the pulp. It remains to add that oil exhibits a preference for certain kinds of metallic particles, so that it attaches itself readily to them, while passing the particles of gangue. The latter, therefore, are quickly wetted by the water, and sink. The oiling of the metallic particles enables them to resist wetting and lessens their specific gravity so that in the presence of sufficient oil they are enabled to float.

3. **Bubble-levitation.**—This phase of flotation depends upon the aid of bubbles of gas, which, by attaching themselves to particles of mineral, buoy them to the surface, like cork belts or the bladders that children use when learning to swim. Various gases have been tried, but air is now generally used for the making of bubbles. The attachment of the bubbles to the metallic minerals in preference to the gangue has been said to be due to an affinity or selectiveness, like that of the oil, and the presence of oil is said to enhance it, but the oiliness of the bubble-film is now believed to be the chief factor.

In order that the bubbles generated in, or introduced into, a pulp may perform their metallurgic function they must last long enough to carry their freight not only to the surface but over the edge of the containing vessel. They must not burst untimely. This necessary prolongation of bubble-life is effected by lowering the surface-tension of the water, of which their envelope or film is composed. The bursting is due to the contractile force of surface-tension, and it must be moderated if the bubble is to last long enough. A decrease of surface-tension is produced by putting some impurity or contaminant in the water. Heretofore oil has been the contaminant chosen, as soap is used by a school-boy to blow his bubbles, he having discovered that the bubbles blown in pure water are too fragile for his play. The

use of oil was inherited from the prior art, but other reagents are likely to be found adequate for the purpose.

Thus the third and most successful phase of flotation has grown out of the second, although it is more nearly the logical development of the first phase. Film-suspension involves the aid of air, for the floating of pulverized minerals on the surface of water is helped by the air entrained in the ore. The attempt to invent an effective method out of oil-buoyancy instead of film-suspension goes far to explain the delay that marked the development of this metallurgic process.

Early Attempts

The story of the slow and toilsome development of this metallurgical process may claim to be "historical" if only for the fact that the use of oil for collecting metals was mentioned by Herodotus. The recovery of gold from the mud of a lake by means of feathers daubed with pitch and held in the hands of apocryphal virgins is as pertinent to the subject as the yarn, 2000 years later, of a young school-teacher in Colorado who was washing oil-stained ore-sacks in her brother's assay-office when she noted that the pyrite floated on the water contaminated by the oil. We know now that the Carrie Everson fabricated in the course of litigation is a myth and that while there was a lady of that name, she was the wife of a Chicago doctor. Indeed, there is reason to believe that Dr. William K. Everson, of Chicago, not his wife, was the originator of the method that was patented. The death of the husband—the real inventor—prevented the development of the process, which fell into the hands of less competent persons, Thomas Criley and Charles Hebron, in collaboration with whom Mrs. Everson devised a method based on "the chemical affinity of oils and fatty substances for mineral particles" [3] and obtained a patent in 1885. She and her husband did ascertain that "acidification of the ore-pulp is necessary for the sharp oil-differentiation of mineral from gangue." [4] But the

[3] As stated by her son. "Carrie J. Everson and Flotation," *M. & S. P.*, January 15, 1916.

[4] H. L. Sulman, Presidential address. Trans. I. M. & M., Vol. XX, page 14.

method patented by her in 1885 was a complete failure as a metallurgical process, although it probably did serve to suggest some of the later investigations and it was used freely in the attempt to disprove the originality of subsequent inventions. The odds were greatly against Mrs. Everson: she was a woman, her idea seemed absurd, she had no mechanical ingenuity herself nor was any at her command, and she had no financial backing. If we consider these circumstances, we shall not wonder at her failure to develop a concentration process.

The first patent employing oil for a metallurgical purpose was that obtained by William Haynes in England in 1860. This is of academic interest as being a prelude to flotation. By mixing coal-tar and resin with crushed ore, in the proportion of 5 : 9, he made a " dough " that held the metallic particles, while the gangue was removed by the help of water and " frictional trituration." The idea proved wholly impracticable and is only worthy of mention as the first recorded use of oil—an oil partly soluble—in the concentration of ores. The next attempt is that of Hezekiah Bradford, an American, who in 1885, two months before the date of Mrs. Everson's patent, obtained a patent for the first method that was based upon a recognition of the surface-tension of water in contact with air. His method was one for " saving floating materials in ore-separation," such as escaped from arrest by tables, vanners, and jigs. He stated:

" These floating particles appear to possess some peculiar quality which repels water from their surface, especially when such particles are exposed even momentarily to atmospheric air, and when such exposure takes place the water is repelled from a sufficient portion of their surfaces to cause such particles to float off on the surface of the waste water from the other particles that sink in the water."

He had the germ of an idea pregnant with metallurgic possibility, but it was still-born. Haynes and Bradford had inklings of the physical phenomena underlying the flotation process, but they were pioneers that blazed no trail and crossed no range of fruitful discovery. Carrie J. Everson comes next in point of time. Her groping after a practical process is noteworthy by

reason of the introduction of acid, but her trail also stopped at the foot of the talus on the slope of the range. The patent records disclose other abortive attempts in the same direction during the ensuing decade, but none is of any consequence except H. L. Sulman's British patent of 1893, in which he describes a means for saving " float " gold by adding something to the mill-water that will diminish its surface-tension. This is interesting as recording scientific curiosity concerning the physics of flotation on the part of a metallurgist who was destined to contribute so greatly to the decisive development of the process. His successful participation is due, in part, to his having been formerly engaged professionally in the chemistry of the oil and soap industries, for thereby he acquired knowledge of a kind that proved of great value to him at a later date.

So far no workable method had been invented—only ingenious schemes and impracticable proposals.

The next incident in this story brings us to the edge of real achievement. In 1894 George Robson, for himself and Samuel Crowder, patented a process for separating sulphides from gangue. He disclaimed " the use of acid or salts and also the method of washing away the gangue with water," and appears therefrom to have been aware of the earlier patents. He effected " the separation of the metallic matter by the mixture of oils alone." Thus he followed in the track of Haynes. The proportion of oil was large: as much as three times the weight of ore. It was a method of buoying the sulphide particles with oil. The process was tried on a working scale at the Glasdir gold mine in Wales and was commended by James Brothers, a firm of experienced metallurgists. But it did not succeed and apparently led nowhere. Yet it opened the way for a decisive event, namely, the technical participation of the Elmore brothers.

Elmore

Francis Edward Elmore was a trained engineer with an inventive mind. His father, William Elmore, bought the Glasdir mine from Samuel Crowder, in 1896. The conventional concentrating

plant, of jigs and shaking tables, had proved unable to make a good recovery of the gold-bearing chalcopyrite in the ore from this Welsh mine. The elder Elmore sent his two sons, Francis Edward and Alexander Stanley, to investigate. It has been stated [5] by Stanley Elmore that, on the occasion of one of their visits to the mill, his brother Frank noticed copper-pyrite adhering to the oil that had dropped from a shaft-bearing, and thus obtained the idea of his invention: "Finely-divided wet copper-pyrite would adhere to a greasy surface, whereas finely-divided wet rock would not." But no accidental demonstration of the action of oil was necessary to arouse Mr. Elmore's interest in face of the fact that Robson had conducted experiments in oil-flotation on the same spot. We have the testimony of Mr. Crowder himself,[6] now a very old man, that Robson's experimental oil-concentration plant was on the mine when it was purchased by William Elmore, and we know also, from Mr. Crowder, that he wrote to Stanley Elmore in 1897 urging him to use oil as a means of concentration. In 1898 Frank Elmore obtained his first patent. A working unit of full size was erected at the Glasdir mine. Walter McDermott, Hennen Jennings, and Wernher, Beit & Co. gave the Elmores their financial support and formed a syndicate, which became known as the Ore Concentration Syndicate.[7]

In his patent Frank Elmore describes the process as "mixing the pulverized ore first with water in considerable quantity, then adding to the mixture an oil of the kind described, which adheres to the metallic constituents but not to the wet rocky constituents." He used a thick oil and introduced the idea of the freely flowing pulp as against the mixing of oil with crushed ore in the presence of only a small proportion of water, as Robson and Crowder had done. By using more water, he also entrained more air, so essential to success, although he did not then recognize this fact.

[5] *M. & S. P.*, September 23, 1916.

[6] *M. & S. P.*, February 24, 1917, and June 16, 1917.

[7] In 1905 it acquired the Elmore vacuum patents and became the Ore Concentration Company.

In the first plant, at the Glasdir mine, the mixture of crushed ore and water was fed at the upper end of a slowly revolving drum, provided with annular helical ribs and transverse blades, so as to mix the pulp and oil without producing emulsification. The oil was introduced through a separate pipe. The mixture was discharged into a V-shaped vessel, where the water and sand subsided, while the oil buoyed the sulphide particles to the top. An oil-residuum of 0.89 specific gravity was used in equal parts by weight with the ore, ton for ton. The oil was so viscous as to require the aid of small rotary pumps to move it forward. The temperature of the oil and water was kept between 54° and 57° F. The loss of oil was 2 gallons per ton of ore. A concentration of 14 : 1 was achieved with a recovery (in the concentrate) of 69% of the gold, 65% of the silver, and 70% of the copper from chalcopyritic ore assaying 1.12% copper, 0.049 oz. gold, and 0.8 oz. silver per long ton. These details are taken from a paper by C. M. Rolker read before the Institution of Mining and Metallurgy, on April 25, 1900. Mr. Rolker described the process as "somewhat dirty and nasty," but he stated that "the mechanical contrivances brought into action by the inventor are excellently adapted to the work demanded, and bespeak very careful thought, as well as patient, systematic, and highly intelligent work."

The discussion of Mr. Rolker's paper, as recorded in the Transactions of the Institution, shows clearly that nobody at that time recognized the part played by air in the process of flotation. Stanley Elmore has cited the use of a Gabbett mixer, which causes a violent agitation with indrawing of "large quantities" of air [8] as proof that he and his brother were "quite cognizant of the fact that it was the air entrapped in the bulk of the oil which rendered it capable of carrying more than its theoretical load of concentrate." But this use of the Gabbett machine was made in 1902, by which time the action of air had begun to be understood. During the discussion of the Rolker paper, two years earlier, nobody present had been able to explain why the actual load of concentrate had been 150% more than was account-

[8] *M. & S. P.*, September 23, 1916, page 452.

eration of hydrogen and probably of carbon di-oxide also, if the pulp contained either calcite or carbonates of the metals.

Potter and Delprat were mistaken in the reactions that were supposed to follow the introduction of the acid, whether it was the sulphuric, the nitric, or the sodium bi-sulphate that they used variously. At that time it was believed that the sulphuric acid reacted with the sulphides to form hydrogen sulphide without attacking the gangue.[10] Then it was suggested that carbon di-oxide was generated by decomposition of a carbonate encrustation on the sulphides, due to weathering of the ore, arguing therefrom that it was necessary for the gas to be produced at the surface of the sulphide particles. Such explanations overlooked the simple fact that the Broken Hill ore contains a considerable proportion of carbonates, notably calcite, siderite, and rhodocrosite. From any of these a warm acid solution would release the carbon di-oxide gas that promptly attached itself to the surface of the metallic particles.

The processes of Potter and Delprat have been labeled under "acid-flotation" and "surface-tension" methods. In their original form, it is true, they did not include the use of oil, and the apparatus pictured in Delprat's patent (U. S. No. 768,035) suggests the surface-tension method of Bradford, but the use of a baffle "to insure the total immersion of all particles of ore in the fluid or liquor" indicates that surface-tension in its simplest form, as used later by H. E. Wood, for example, was not a principal agent. In Potter's apparatus—a pointed box—the feed has to pass under the surface and is wholly submerged, so that surface-tension again is not given free play, although, of course, it is a factor in the formation of the bubbles that buoy the sulphides to the surface after the pulverized ore has been mixed thoroughly with the acidulated water.

In August, 1904, Auguste J. F. De Bavay patented a process resembling that of Bradford. He used neither acid nor oil, depending entirely upon the effect of surface-tension to form a film of sulphide particles while allowing the particles of gangue to sink.

[10] "The Physics of Ore Flotation," J. Swinburne and G. Rudorf, *M. & S. P.*, February 24, 1906.

The company formed to exploit his patents claimed that the process worked without either oil or acid, but it was admitted that the flotation was improved thereby, and both oil and acid were used at a later date. In 1910 his rights were transferred to Amalgamated Zinc, Ltd., and in 1912 this company was annexed by Minerals Separation, Ltd. De Bavay's method was employed on a large scale at the North Broken Hill mine and in a plant for treating the dumps of the South and Block 10 mines. It is also used on current zinc-tailing produced at the North and South mines. Treatment is confined mainly to material free from slime. Indeed, none of the earlier processes, the Potter, Delprat, De Bavay, Cattermole, or Elmore did good work on slime—at Broken Hill.

The operation of some of these Australian methods of flotation without oil is an interesting feature. Most of them treated old dumps and it is well to note T. J. Hoover's suggestion [11] that "there may be organic substances in the ore which, upon the addition of acid, yield gummy organic compounds that selectively adhere to the ore." The research of recent years has disclosed the fact that a large variety of soluble frothing-agents are effective and that a number of shrubs yield derivatives capable of replacing oil in the flotation-cell.

In 1903 a Potter plant was erected to treat middling from the lead concentrator on Block 14.[12] Concurrently the Delprat process was adopted by the Broken Hill Proprietary, the plant being increased successively from its original capacity of 3500 to 6250 tons per week. Litigation ensued between these two Australian patentees. This ended in a compromise whereby Potter was eliminated; but it is worthy of note that Potter's method was the first flotation process to be used successfully on a working scale.

In 1905 the Zinc Corporation was formed to purchase and treat several large dumps. In 1906 the Potter process was used by this company on the British Broken Hill Proprietary dump,

[11] "Concentrating Ores by Flotation," page 101.

[12] The superintendent of this mill was Henry Lavers, whose name is notable in the history of the process.

from which a concentrate was obtained containing 44% zinc, 8% lead, 8 oz. silver, representing a recovery of 81% zinc, 55% lead, 55% [13] silver, at a cost, including transport, of 50 cents per ton. H. C. Hoover testified in court that the Potter process, as used by the Zinc Corporation, "proved a commercial failure; for the later results, after the mill was remodeled, were not as good as those just quoted." In 1907 the Minerals Separation process was adopted in a plant erected under the direction of the patentees, but, as Mr. Hoover says, it "also proved a failure,[14] and after exhaustive trials the Elmore flotation process was introduced and found successful." He refers, of course, to the Elmore vacuum process, which was used by the Zinc Corporation chiefly on jig-middling from the Block 10 mill, until 1910, when, on the advice of his brother, T. J. Hoover, the improved Minerals Separation process was substituted, because it promised to give better results on slime and because most of the coarse material of the tailing dumps had been milled by that time.

As early as 1902, while working with the granulation, or Cattermole, process in the Central mill, the scum of slime made from re-crushed tailing was saved by floating it over a spitz-box. W. Shellshear and F. A. Beauchamp suggested the application of this idea to correct the failure of the granulating process caused by floccules of mineral breaking away from the granules on the tables. The suggestion was put aside until 1903, when a small spitz-box was tried. It was ascertained that the flotative effect was produced while using 9 lb. oil and 22 lb. acid per ton of ore. The proportion of oil was decreased gradually to 2 lb. per ton. This was the real beginning of froth-flotation.[15]

The first mill to use the Sulman & Picard modification of the agitation-froth process, as recorded in U. S. patent 835,120, was the one at the Central mine, built in 1905, as previously men-

[13] These figures refer to the final test made by W. E. Simpson on a mixture of tailings from all the dumps owned by the Zinc Corporation.

[14] Partly because the plant was overloaded to about double its capacity.

[15] It has been asserted that this method was discovered by the mill-men in the Central plant at Broken Hill and that the M. S. representative then cabled to the London office about it. The account given by Mr. Hebbard is not contradictory.

tioned. In 1907 a new mill was finished and by 1908 the recovery had been improved to 85.5% of the zinc, 82.5% of the lead, and 83.8% of the silver, on a material assaying 21.4% zinc, 6% lead, and 8.6 oz. silver per ton, yielding a concentrate assaying 42.5% zinc, 11.4% lead, and 16.6 oz. silver per ton. Concentration was in the ratio of 7 : 3.

FROMENT

The scene shifts from Australia to Italy. At the time when Potter and Delprat introduced their methods at Broken Hill, another investigator was about to contribute his quota to the development of flotation. The Elmore bulk-oil method had been seen by Alcide Froment at the Traversella mine, in Italy, where he was engaged as an engineer in 1901, when he invented what he himself termed " a modification of what is known as the oil process of concentration." His modification—patented in June, 1902—was to introduce a gas into the freely flowing oiled pulp used by Elmore. He argued, in his patent, that " if a gas of any kind is liberated in the mass the bubbles of the gas become coated with an envelope of sulphide and thus rise readily to the surface of the liquid where they form a kind of metallic magma." The phrase " gas of any kind " is important, for, although he generated his bubbles of gas by the reaction between sulphuric acid and the carbonates of the gangue or between the acid and the limestone that he added to the pulp, he hit upon one of the fundamental principles of the flotation process as we know it now. If he had specified air as the particular gas to be used he would have been acknowledged as the pioneer of present-day flotation. Air was present, of course, and played an important part in the operation, for in his description he specified the use of a centrifugal mixing device " in which two stirrers work in opposite directions, making 300 revolutions per minute." In his patent he explained that " the sulphide particles when moistened by a fatty substance " have a tendency " to unite as spherules and to float upon the surface of the water." He stated also that " the rapidity of the formation of the spherules and their ascension is in

direct ratio to the quantity of gas produced in a given time." As to oil, his patent mentions " a thin layer of ordinary oil," but in the instructions given by him to the Minerals Separation people he specified as little as " 1% of oil for ore containing up to 5% of metals " and up to 3½% " for ore containing 50% of metallic lead."

Minerals Separation

Before proceeding further it will be necessary to trace the origin of Minerals Separation, Ltd. At the end of 1901, John Ballot, W. W. Webster, and James Hay formed themselves into a syndicate to take an option on the Australian rights to the Elmore bulk-oil process. They engaged the firm of Sulman & Picard to act as advisory metallurgists. Acting on their advice, the syndicate did not exercise the option. In December, 1902, John Ballot purchased the patents of Arthur R. Cattermole and assigned them to his syndicate, which became known as the Cattermole Ore Concentration Syndicate. On December 31, 1903, this syndicate was succeeded by a company, called Minerals Separation, Ltd., the directors being John Ballot, J. H. Curle, W. W. Webster, S. Gregory, H. L. Sulman, and H. F. K. Picard.

Now we return to Froment. His work appears to have been unknown in England until an abstract of his British patent was published in the Journal of the Society of Chemical Industry and was seen by Mr. Sulman in August, 1903. Whereupon negotiations for the purchase of Froment's patent were opened by Mr. Ballot. He went to Milan to meet Froment, who, on November 7, 1903, sold his rights for £225. On December 29 Froment sent some drawings, with descriptions and instructions explaining his mode of operation. Early in 1904 a small plant designed by him was forwarded to London, but the apparatus was discarded, and destroyed subsequently, by the Minerals Separation people. Froment was in poor health at that time, and he died soon afterward. His patents had been taken out in Great Britain and Italy, but not in the United States, and when Mr. Ballot acquired them it was too late to obtain American

rights, more than a year having elapsed since the grant of the British patent, on June 9, 1902. So the Froment patent was set aside as of no immediate value.

Cattermole's patents had been duplicated in the United States. In his American patent, No. 777,273 of September 28, 1903, Cattermole prefaces his description by reference to the selectiveness of oil, when emulsified, for sulphide particles, such selective action being intensified by acidulation of the water. He then proceeds to say that if the mixture be agitated thoroughly there is a tendency for the metalliferous particles, now well coated with oil, to adhere together, forming "granules" that sink and are readily separated from the lighter gangue by an up-current of water. In his description of the operation he says that "the granules, with a certain amount of heavy sands, sink to the bottom and are discharged (see Fig. 1) through a pipe G^1 into the vessel A^5, while the lighter sands are carried away by the upward current and discharged through outlet G^2 to a light-sands tank J." In the drawing, A^1, A^2, A^3, A^4, A^5, and A^6 are mixing-vessels; G and K are classifiers; E is a tank containing oil-emulsion. He refers to the proportion of oil several times in vague terms, explaining, however, that it should be insufficient to materially lessen the specific gravity of the metalliferous mineral particles." Finally, he specifies the proportion as "usually an amount of oil varying from 4% to 6% of the weight of metalliferous mineral matter present in the ore." This can be interpreted variously; if it refers to the sulphides to be concentrated, then an ore containing 20% blende would require from 0.8 to 2% of oil, or from 16 to 24 lb. per ton of ore. On the other hand, a 2% chalcocite ore would need only 1.6 to 2.4 lb. of oil per ton of ore, which is as little as is now used. Such was the method from which patent 835,120 of Minerals Separation is claimed to be a logical development.

Much of the early experimental work of Minerals Separation was done in the laboratory of Sulman & Picard, at 44 London Wall, but in March, 1904, Mr. Ballot established his own laboratory on Aldermanbury avenue, and it was there that decisive results were obtained. In 1903 a model 50-ton plant, to use the

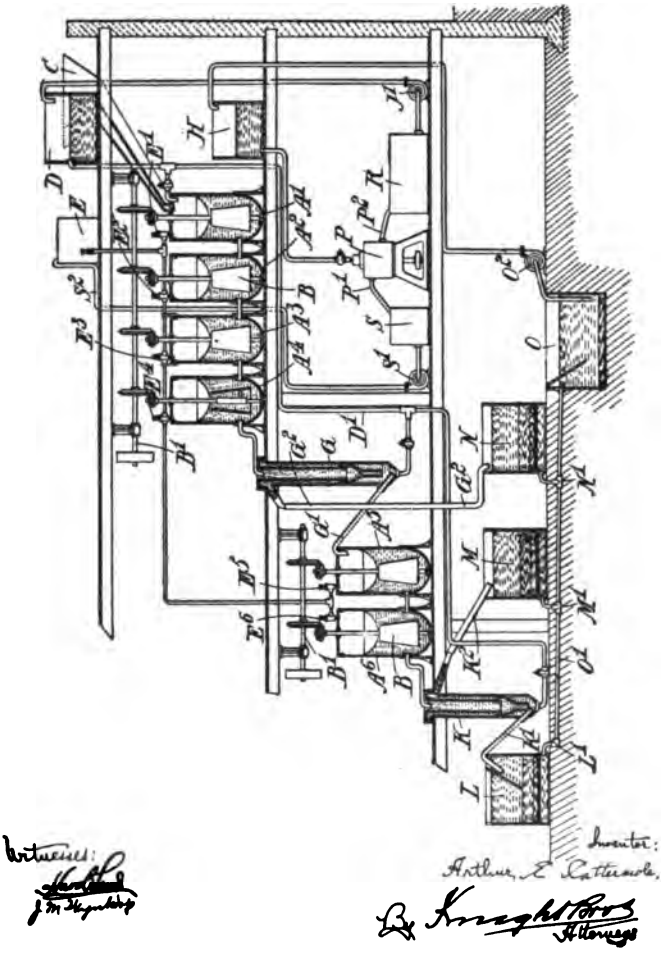
No. 763,259. PATENTED JUNE 21, 1904.

A. E. CATTERMOLE.

CLASSIFICATION OF THE METALLIC CONSTITUENTS OF ORES.

APPLICATION FILED SEPT. 30, 1903.

NO MODEL.



Witnesses:

Inventor:
Arthur E. Cattermole,
By Knight Bros
Attorneys

FIG. 1.—The Cattermole Patent.

Cattermole process, was constructed and sent to the Central mine at Broken Hill, Australia.

The Minerals Separation people, notably the chief metallurgists, Messrs. Sulman and Picard, were experimenting with Cattermole's method and trying to develop a workable process at the time when their attention was called to Froment's patent. When they acquired this patent, they made experiments in accord with the specifications and the later instructions sent by Froment. To the detached spectator it would seem more logical to assume that Froment's floating "spherules" rather than Cattermole's sinking "granules" would lead to something like the froth-flotation process of today. But that is not the story told in the courts of law. The metallurgists identified with Minerals Separation testify that they had discarded Froment's patent and his instructions, having found them worthless, and were trying various modifications of the Cattermole method when suddenly they happened upon the particular combination essential to the froth-agitation process. Messrs. Ballot, Sulman, and Picard agree in stating that protracted experiments were being conducted in their London laboratory under the immediate charge of Arthur H. Higgins, who had been instructed to try all sorts of variations in temperature, acidulation, oiling, and mixing. Nothing noteworthy happened until the proportion of oil was reduced, whereupon the "granules" began to rise instead of sinking and "the quantity of floating material increased rapidly when the oil was reduced below a certain point, this point being 0.62% of the oleic acid on the ore." So testifies Mr. Ballot. Thus happened "the startling discovery of the agitation-froth process," according to W. H. Ballantyne, Mr. Ballot's patent lawyer. The date was March 3, 1905. Then followed the British patent No. 7803 of April 12, 1905, and the American duplicate, No. 835,120—the date of application being May 29, 1905, and the date of issue November 6, 1905.

Before leaving this part of the story it is worth noting that the Cattermole 50-ton plant, already mentioned, had been erected in the Central mill early in 1904, and experiments were made there under the direction of G. A. Chapman. Tests

showed that when using 0.75% of oil on the ore "the results were excellent, with all float concentrate, no granular material being formed." So says James Hebbard, the manager of the Central mine.[16] The adjective "excellent" is used in the light of later events, for floating of the mineral was incompatible with the granulation upon which the Cattermole process depended. The importance of the floating does not seem to have been appreciated until a year later—early in 1905—when "a remarkable development in the operation was discovered (strangely enough, at the same time here [Central mine] and in the Patent Co.'s [Minerals Separation] laboratory in London), which had for its main principle the reversal of all previous operations, and consisted in the complete flotation of each particle of mineral independently in place of granulating the mineral particles and causing them to sink, thus not only revolutionizing the process, but greatly simplifying and cheapening it. The developments noted were mainly along the line of decreased consumption of oleic acid, for example, from 3% oleic on ore, resulting in very little float, down to 1%,[17] giving practically a complete float." According to this, the Higgins "discovery" was made independently and contemporaneously at Broken Hill, but the underlying principle was detected a year earlier by Mr. Chapman, who had experimented with the Froment process in the London laboratory of Minerals Separation during 1903—again the suggestion that Froment had pointed the way to the agitation-froth process.

Next we revert to the first contact between the Elmore brothers and the Minerals Separation people. As already mentioned, in 1901 the Ore Concentration Syndicate gave Messrs. Ballot, Webster, and Hay an option on the Australian rights to the El-

[16] Proceedings Aust. Inst. of M. E., November 10, 1913. The same engineer relates how, before 1901, "it had been long observed that a froth was formed containing high metallic values, in silver and lead particularly, whenever conditions were favorable, as for instance, where the rotation of trommels, or the splash of the elevators or raff-wheels, or the motion of the jig-plungers, produced a violent agitation of the mill-water containing slime." The use of oil tended to make such froth more persistent. I have mentioned the suggestion made by Beauchamp and Shellshear in 1902 while at work in this same mill.

[17] Not below 1%, apparently.

more bulk-oil process. In accordance with this agreement, Mr. Ballot and his associates sent ore to be tested at the Elmore laboratory, to which they had free access while the experimentation was in progress. In the agreement it was stipulated that the holders of the option " and their assigns " should notify the Elmore syndicate of any " improvement, addition, or discovery " that they might make and the Elmore syndicate was " to be entitled to every such improvement, addition, or discovery whether the same shall be patented or not."

Mr. Ballot and his associates made tests and held the option for 11 months, that is, until late in 1902. Messrs. Sulman and Picard were engaged by Mr. Ballot to supervise the tests. They were " treated with the greatest frankness," says Stanley Elmore. The option was not exercised. Then followed Mr. Ballot's purchase of the Cattermole patents and in the succeeding year the acquisition of the Froment and Sulman & Picard patents, followed immediately by the organization of Minerals Separation, Ltd., as a process-exploiting company. In 1905 the Elmores brought suit to enforce the clause above quoted, in the agreement of 1901, claiming that they were entitled to the benefit of the improvements following upon the insight into the process given to the Minerals Separation people during the tests made under the option. The case went against the Elmores, the Court of first resort deciding that the particular clause had been introduced into the contract without sufficient authority after it had been signed. In the second trial, Messrs. Ballot, Hay, and Webster presented evidence to show that the Cattermole and other patents had never been in their possession but had passed from the inventors through a trustee to the syndicate that became Minerals Separation, Ltd. Whereupon the proceedings were stayed. The affair left a feeling of bitter animosity between the two factions; the Elmores showed so keen a sense of betrayal as to resign from the Institution of Mining and Metallurgy when Mr. Sulman was nominated for the presidency of that professional society in 1911. This incident indicates the bitterness, rather than the merits of the quarrel, but it must be recorded in this history of the process because it helps to explain the acerbity of

the litigation that ensued and that still animates the protagonists in this metallurgical vendetta.

For three years, from 1906 to 1909, the Elmores fought the Minerals Separation's attempt to hold a patent in Germany. The patent was granted, but it was annulled subsequently by a higher court.

In 1907 Minerals Separation brought suit against the Ore Concentration Company, alleging infringement of Froment's patent, but in 1909 the Minerals Separation company discontinued the action, paying costs.

In 1909 the Elmores and the British Ore Concentration Syndicate brought suit against Minerals Separation for infringement of Frank Elmore's bulk-oil patent of 1898 and Stanley Elmore's patent of 1901, specifying the use of acid in the bulk-oil process. They lost in the first court, they won on appeal, but lost on final resort to the House of Lords. Both the use of oil and of acid were held to have been anticipated, and the Minerals Separation froth-agitation process was held to be entirely different from the bulk-oil method. Subsequently a new suit was started in Australia, the claim of infringement against the Sulphide Corporation, a licensee of Minerals Separation, being based on acidulation. The Australian court decided against the Elmores, who appealed, unsuccessfully, to the Privy Council, in 1914.

Air-agitation Methods

It is important to note that these suits dealt only with the bulk-oil patents of 1898 and 1901, and had no reference to the vacuum process of 1904. To the agency of gas in flotation we now return. So far the fact that bubbles of air would do the work of bubbles of chemically generated gases had been overlooked. In September, 1903, Sulman & Picard described the use of air " or other gas " in British patent No. 20,419, which was duplicated in the United States as No 793,808. In this they pictured a perforated coil of pipe through which either air is introduced into pulp with which oil has been already mixed or air and oil are admitted simultaneously in the form of a spray.

The latter scheme has not proved practicable, whereas the procedure in which the oil is previously mixed with the pulp and then subjected to aeration by the introduction of air through the perforations in the pipe is a practical method. They said, " The oiled metalliferous particles resulting from either of the processes above described have the power of attracting to themselves with a greater comparative strength than the gangue particles, the films or bubbles of gas which exist in the mass and are thus raised to the surface of the liquor by gaseous flotation." They did not claim the use of air as a discovery and they seem not to have known how near they were to the later phase of flotation, in which the making of a multiplicity of air-bubbles, or " froth," is the principal feature.

In June, 1904, Frank Elmore applied for a patent to use electrolysis in order to generate gas in a freely flowing pulp, and in August of the same year he obtained British patent No. 17,816, in which he described the performance of flotation in a vacuum, so as to liberate " the air or gases in the milling water." Thus six years after the date of his first bulk-oil patent Elmore had learned to put the air to purposeful use. He subjected the oiled and acidulated pulp to a vacuum, thereby releasing the 2.2% of air normally absorbed in water. By lowering the pressure and raising the temperature this air is released, thereupon attaching itself, in the form of bubbles, to the oiled sulphide particles, which rise to the surface. For example, the air in a ton of pulp consisting of 6 parts of water to 1 of ore suffices to lift 360 pounds of zinc-lead sulphides in a Broken Hill ore. In actual practice, however, the weight of sulphides floated is considerably greater than the theoretical proportion as based on the efficacy of the air released from absorption in water. Part of the work is done by the gaseous carbon di-oxide liberated by the reaction between the acid and the carbonates, such as calcite, either in the gangue or added in the form of limestone. But a larger part of the bubbling is caused by the air entangled in the ore particles and entrained in the pulp during energetic mixing. In this process the quantity of oil added to the pulp was reduced from the ton used at Glasdir to 10 pounds per ton of ore, and finally to as little

as 3 pounds per ton of ore. The machine devised by Mr. Elmore for the performance of his vacuum process was remarkably ingenious and to it the success of the process was largely due. It was applied at several Scandinavian copper mines, notably the Sulitelma, and also in the Zinc Corporation's mill at Broken Hill, as already mentioned.

This vacuum method of Elmore was a notable step toward the recognition of the part played by air in flotation, and in so far as he used air in a pulp that had undergone agitation with a relatively small proportion of oil he furnished a metallurgic signpost that pointed to the final success of the process.

Flotation in America

So far flotation had received scant attention in the United States. The old Elmore bulk-oil method had been tried, unsuccessfully, at the Boston Consolidated and Mammoth mines in Utah in 1900 and 1901. In 1906 a surface-tension process of great ingenuity, invented by A. P. S. Macquisten, was used in the Adelaide mill, at Golconda, Nevada, and in 1911 a similar plant was erected at the Morning mine, in Idaho, but these interesting efforts were mere ripples on the calm surface of American apathy, which at the time gave no promise of the full tide of metallurgical advance that since then has swept over base-metal mining in the West.

Another American patent must be mentioned, as linking the Elmore bulk-oil process with the later frothing methods. The patent of Edmund B. Kirby is No. 809,959 of December 14, 1903. He used from 25 to 75% of oil in a flowing pulp; but he depended upon thin oil—kerosene—and violent agitation, so that he departed from the Elmore type of flotation. The more interesting feature of his claim, however, is "the injection of a gas, preferably air, into the mass," which statement, if taken with his reference to "allowing the hydrocarbon-coated particles to float to the surface of the mass," seems indeed to be a forecast of froth-flotation. The patentee—Kirby—himself says: "It is thought that the use of a gas to assist in the flotation of the coated particles . . . is radically new in this art." He adds: "The employment

of the gas in the manner stated brings in a more powerful floating agency than anything before used." How prophetic! His gas was " preferably air." Moreover, he knew of the use to be made of the air " dissolved " in water, as adopted a year later by Francis E. Elmore, for he says: " The air-bubbles not only tend to attach themselves directly to the coated particles, and thus float them to the surface, but the air becomes dissolved in the water to its maximum capacity. This dissolved air tends to again separate itself from the water and attach itself in minute globules to the coated particles." Mr. Kirby tried his process on a number of British Columbian ores, but no working plant was erected; nevertheless, it is apparent that he has not received proper credit hitherto for his ingenuity, and it is a pleasure to make the correction here.

The credit for bringing the froth process to the notice of the American public belongs to J. M. Hyde, who had been in the employ of a subsidiary syndicate organized by Minerals Separation for the exploitation of flotation in Mexico. Mr. Hyde was introduced to Mr. Ballot by Theodore J. Hoover, who, in October, 1906, had been engaged by Mr. Ballot as technical adviser and general manager for the Minerals Separation company. In 1910 Mr. Hyde went to Mexico and early in 1911 he resigned, at the conclusion of his one-year contract with the syndicate. Shortly afterward he went to Montana, at the instance of H. C. Hoover, to inspect the property of the Butte & Superior Copper Co., this company having offered Mr. Hoover a participation in a bond issue. The business proving unattractive, Mr. Hoover withdrew from it, but Mr. Hyde commenced to investigate the metallurgical problem presented by the zinc-lead ore of the Butte & Superior company's Black Rock mine. After making the necessary tests with the slide machine, he erected a trial plant in disregard of the Minerals Separation patents. This was in August, 1911, and not until the Butte & Superior company had negotiated with E. H. Nutter, the American manager for Minerals Separation, who demanded a prohibitive royalty. In October, 1911, suit for infringement of patent was brought by Minerals Separation against Mr. Hyde.

Meanwhile, in December, 1910, T. J. Hoover had severed his connection with Minerals Separation, after having been instrumental in the successful development of the company's business in Australia and in improving the various apparatus employed in the froth-flotation process, especially in that country. His resignation was accompanied by some friction with Mr. Ballot, into the details of which it is not necessary to go, but the fact is a part of the history of the process. In December, 1912, Mr. Hoover published his book, " Concentrating Ores by Flotation," after a grudging consent had been obtained from his former employers, in return for which he excised parts of the original manuscript trenching too deeply into patent matters. This is recorded here in order to remove the impression, still persisting, that Mr. Hoover wrote and published his book while connected with Minerals Separation.[18]

We now return to Mr. Hyde and the commencement of a big litigation. The suit started against him in 1911 was tried first in the District Court of Montana and judgment was given against him in August, 1913. On appeal, before the U. S. Circuit Court of San Francisco, this judgment was reversed in May, 1914. By writ of certiorari the case was brought before the Supreme Court of the United States, which on December 11, 1916, reversed the decision of the Appellate Court and decreed that patent 835,120 was valid, but confined the scope of the patent to violent mechanical agitation, the use of less than 1% of oil, and a persistent kind of froth.

It is worthy of note that the first successful froth-flotation plant erected in the United States, by Mr. Hyde in 1911, did not start until six years after the grant of patent 835,120 and not until 20% of the world's production of zinc was being made by aid of the group of other flotation processes in use at Broken Hill. This may be compared with the statement of the U. S. Supreme Court, in its final review of the Hyde case, that " the process in

[18] In mentioning these and other personal incidents, like the Elmore-Sulman & Picard affair, I am prompted solely by the desire to state facts essential to a correct understanding of the conditions governing the patent litigation, because they played a decisive part in the technical development of the process.

suit promptly came into extensive use for the concentration of ores in most, if not all, of the principal mining countries of the world, notably in the United States."

The first successful application of the froth-flotation process in the United States was made at Butte, on a zinc-lead ore, as we have seen. The later development of the process has been based on the treatment of copper ores, especially the chalcocite disseminated in the immense orebodies disclosed in Arizona, Utah, and Nevada. This part of the story begins with the tests made by Minerals Separation in their London laboratory and in plants erected at sundry copper mines in other countries, such as the Caucasus Copper and the Great Fitzroy, with results generally poor. In his book, dated July 4, 1912, Mr. Hoover refers to the limitations of the process and says:[19] "The fourth limitation is one for which at present no adequate reason can be given. An ore in which the valuable minerals are wholly or partly bornite or chalcocite, as those of Bingham canyon, will probably give trouble to flotation processes, although not always, for among the many ores tested the one which gave the most uniformly satisfactory results was a copper ore assaying 2.8% copper, all in the form of microscopic specks of bornite." He proceeds to remark: "It may be that only those ores where bornite and chalcocite are of secondary occurrence give trouble." In Mr. Hyde's report of January 8, 1911, given as an exhibit in the lawsuit, it is stated that the tests carried out in the Minerals Separation laboratory proved that "the copper ores of a good part of the Southwest and also of at least a portion of the Utah region contain chalcocite, *which is not floatable by any of the methods so far tested.*" This summarizes the opinion held by the Minerals Separation staff at that time. However, they discovered their mistake two years later. Tests on chalcocite ore from the Inspiration mine, in Arizona, were made in Mr. Nutter's laboratory at San Francisco during 1912, but the results were not good enough. At the end of that year, however, an 87% recovery on a 2% copper ore was obtained in a 15% concentrate. The telegram sent to the New York office of the company was mutilated

[19] "Concentrating Ores by Flotation," first edition, page 157.

in transit so as to state that a 50% concentrate had been obtained, and premature rejoicing followed.[20] Nevertheless the Minerals Separation staff promised good results and erected a 50-ton experimental plant at the Inspiration mine. The company took out a license early in 1913. On March 23 an experiment on low-grade chalcocite ore was made by T. A. Janney at the Arthur mill of the Utah Copper Company. This proved satisfactory. During the same month, March, 1913, the Minerals Separation staff, at the Inspiration mine, had demonstrated a 90 to 92% recovery and a 35 to 40% concentrate on a 2% ore, with a 0.15 to 0.2% tailing. The presence of a colloidal kaolinized mineral diverted the oil from its proper function and interfered with the recovery of copper until G. A. Chapman suggested the addition of the oil to the ore in the tube-mill, where the metallic particles became oiled at the instant of exposing fresh fractures. These experiments warranted the expectation that on a 1.58% ore there would be obtained a 27½% concentrate with a recovery of 92% and a tailing loss of only 0.13%. A 600-ton Minerals Separation test-plant was erected in January, 1914; in July of that year a pneumatic equipment consisting of five Callow cells and one Pachuca tank was added and between August and October a Towne machine was introduced. In 1915 the Inspiration Consolidated Copper Co. built a mill of 18 sections, each of 800 tons capacity, or a total of 14,400 tons daily. Since then this mill has treated as much as 21,000 tons in a day.

In June, 1914, Mr. Chapman started flotation experiments at Anaconda in a 200-ton plant, obtaining 90% recovery. On February 1, 1915, the Anaconda and Inspiration companies signed a contract with Minerals Separation by the terms of which they agreed to pay royalty on a sliding scale ranging from 12 cents per ton on 4000 tons daily to 4 cents per ton on the treatment of more than 30,000 tons daily. By a curious proviso in the contract no royalty was payable on the 5000 tons between 10,000 and 15,000 tons daily. The tonnage coming under the terms of this agreement included the ore treated by sundry subsidiary companies, the consequence being that the maximum

[20] *M. & S. P.*, March 18, 1916.

tonnage and minimum royalty specified in the agreement were reached by the close of 1916, at which time the Anaconda flotation plant was treating 14,400 tons daily. As an example of the saving made by aid of flotation, it is worth mentioning that whereas the tailing from the water-concentration mill used to assay 0.62% copper, the residue now after treatment in the flotation annex assays only 0.15% on a 3% ore; that is, out of 60 pounds of copper per ton only 3 pounds goes to waste, as compared with 12.4 pounds formerly. The recovery is 95%. Moreover, the metallurgical improvements made at the Washoe plant during 1915 were so effective as to enable an increase of 55,000,000 pounds per annum to be made in the production of the Anaconda company "without increasing the tonnage or grade of ore that has been mined in the past." So testified Mr. John D. Ryan, the president of the company, in his annual report.[21] Further, he stated that "approximately 40,000,000 pounds of this increased production will be made without adding to the cost per ton of ore treated." This is the equivalent of the output from a big mine.

Meanwhile preliminary tests had been started at the Miami mine, which is a near neighbor of the Inspiration. From December, 1913, to August, 1914, the testing was directed by R. C. Canby, who used various types of apparatus, notably the Minerals Separation and Towne machines. On August 7, 1914, a pneumatic flotation plant was erected. The remodeled mill, having a capacity of 4200 tons, went to work on March 15, 1915. On July 14, 1914, Minerals Separation brought two separate suits based on patents 835,120 and 962,678, but these suits were dismissed on request of Minerals Separation, and on October 10, 1914, a single suit was started for infringement of three patents, the two already mentioned and No. 1,099,699.

Instead of using the blade-impeller type of agitator, the Miami Copper Company adopted the Callow machine, essentially a sloping launder with a canvas bottom through the pores of which air under small pressure is admitted into the pulp previously oiled. Such oiling of the pulp was aided at first by the use of a Pachuca tank, but in the spring of 1915 this type of agita-

[21] *M. & S. P.*, February 26, 1916.

tor was found superfluous and since then the oil has been simply added to the pulp while flowing through a launder to the flotation-cell. In the trial of the suit before the District Court of Delaware, the defendant claimed that he was not using the agitation-froth process of patent 835,120 but a bubble method similar to that of patent 793,808, which was granted to Sulman & Picard on July 4, 1905, on an application dated October 5, 1903. In this patent a perforated coil of pipe is described, the idea being to admit air and oil in the form of spray, so that the globules of oil attach themselves to the metallic particles in the ore and float them to the surface. The pneumatic machine used at Miami was devised by J. M. Callow and patented as No. 1,104,755 of July 21, 1914. The idea had been used already in T. J. Hoover's British patent No. 10,929 of 1910. Mr. Hoover's patent was not duplicated in the United States and Mr. Callow was unaware of it. Another investigator, R. S. Towne, had patented the idea previously, in the form of a carborundum wheel, the central hole of which he plugged, so that the wheel served as a porous medium. The admission of air to make froth, without the aid of mechanical agitation, was developed in several machines at a later date—in 1915 and 1916—as has been duly recorded in the technical press.[22] The kind of froth produced by blowing bubbles of air through the pulp is claimed to be different from that made by beating air into the pulp with a mechanical stirrer; in the one case the froth is said to be thin, tender, and evanescent while in the other the froth is described as thick, coherent, and persistent.

However, the first trial-court decided in favor of Minerals Separation's contention that the Miami Copper Company was infringing its patent, 835,120, and also 962,678. The judgment was delivered on September 30, 1916, an appeal being filed at once by the defendant.

[22] "The Kraut-Kollberg Flotation Machine." By Max Kraut, *M. & S. P.* July 1, 1916. "An Improved Pneumatic Flotation Machine." By James M. Hyde, *M. & S. P.*, November 25, 1916. "The Porous Bottom." By Rudolf Gahl, *M. & S. P.*, September 30, 1916. "Flotation in the Clifton-Morenci District." By David Cole, *M. & S. P.*, October 14, 1916. "Flotation at the Calaveras Copper Mine." By Hallet R. Robbins, *M. & S. P.*, November 25, 1916.

Patent No. 962,678 is important and interesting because it involves an idea to which no reference has as yet been made in this brief history of the process: I refer to the varying solubility of oils and the use of soluble agents for that modification of the surface-tension of water to which the phenomena of froth-flotation or bubble-levitation are so largely due. The idea is not recent. Haynes, in his British patent of 1860, used coal-tar from gas-works in a rudimentary process of oil-flotation. Coal-tar contains as much as 20% soluble products. In U. S. patent 788,247, dated April 25, 1905, Cattermole, Sulman, and Picard used cresol and phenol, both soluble in water, as modifying agents.

On June 29, 1910, Sulman & Picard obtained U. S. patent 962,678 for a " soluble frothing agent," and this is the patent that the Miami company is charged with having infringed by reason of using cresol with pine-oil in its flotation operations. Application for this patent was filed on April 30, 1909. The illustration shows a beater form of agitator and " beating air into the mixture " is specified. Mention is made of " an organic compound in solution " and " amyl acetate " is instanced. No particular proportion of this " mineral frothing agent " is specified and an increase of the soluble substance is held not to interfere with the operation. The decision of the higher court on the validity of this patent will have an important bearing on the future of the flotation process, for it is manifest that the term " soluble frothing agent " is extremely comprehensive and will frustrate legitimate attempts to avoid the embargo on the use of oil. Meanwhile the Supreme Court's recent decision validating the patent on the use of a " critical " proportion of oil, namely less than 1%, has been stultified by successful concentration on a scale of 1000 tons or more per day when using 22 to 23 pounds of oil per ton of ore. At the same time comes the news of the Freeman process, in which soda-cake is being used successfully at Broken Hill as a modifying agent instead of oil. The litigation is far from ended and before it is closed it will be likely that oil will have been discarded in favor of other contaminants capable of lowering the surficial tension of water so as to permit the formation of a metallurgic froth.

In 1914 the flotation of oxidized lead ores became the subject of successful experiment, the method being to sulphidize the exterior of the oxides by means of sodium sulphide. This was accomplished so successfully that an effort was made in 1915 to apply the method to oxidized copper ores, which, however, are not readily amenable because the sulphidization penetrates the ore particles so deeply as to interfere with the differential treatment and to consume an excessive amount of the sulphidizing agent. The treatment of zinc-carbonate ores by sulphide-filming has been even less successful, owing to the fact that such ores contain enough zinc silicate to interfere with flotation.

The story of flotation flows by devious ways and is broken by many cross-currents. Patents serve to record the high-water marks of ingenuity but they fail to disclose the movement between given points, and, what is much more important, they ignore the slow increase of manipulative skill. It is to manipulation, learned empirically in the laboratory and mill, that the flotation process owes its metallurgic success. Given the directions to be found in Kirby's or Froment's patents, the flotation expert of today can produce an effective result, without, apparently, borrowing from any later inventor. That is why the experiments made in Court have proved almost anything it was desired to prove. The manipulation to which success in the mill is largely due contravenes no patent and trespasses no man's preserves. A proof of this is to be found not only in the slow application of the flotation idea in metallurgy but in the delay that marked the fruitful use of the latest phase of the process. The froth-flotation that is claimed to be a new discovery is said to have been discovered in 1905; yet it was not introduced into an American mill until 1911, and even after that event the most skillful engineers, whether in the employ of the patent-mongering company or not, failed to apply it successfully for several years, not until 1914.

Haynes and Bradford left no trail. Everson failed to arrive, but it is likely that her patent put the idea of flotation into the heads of others, for example, Robson. He did not succeed, but he gave the clue to Elmore, who then prompted Froment and

Kirby. Sulman was experimenting with the Cattermole method when he heard of Froment's scheme, and from that, I believe, he got the notion of using air to make a froth. Hoover, Callow, and other technicians, by the patient empiricism of the mill and laboratory, developed a workable process. Such, in brief, I believe to be the true pedigree of the flotation process.

PRINCIPLES OF FLOTATION [1]

By T. A. RICKARD

Introduction.—The understanding of the principles governing flotation has been delayed mainly because the explanation of the phenomena—or appearances—characteristic of the process is to be found in physics rather than in chemistry. Modern metallurgy has been in the hands of men primarily chemists, rather than physicists. Cyanidation and chlorination, for example, may be explained by chemical formulas, even if they cannot be expressed in their entirety by the language of elemental symbols; but flotation is not to be interpreted in that way; it is controlled by physical laws that are obscure and that hardly came within the cognizance of the metallurgist until the need for study was felt by him within a period so recent that the full results of scientific research are not yet available.

To understand the rationale of the flotation process we must return to the amusements of our boyhood; in the soap-bubble and in the greased needle we shall find an inkling of the forces at play in the flotation machine. Everybody knows the trick of the greased needle. If a needle be greased and then placed carefully on the surface of tap-water in a bowl it will float, despite the fact that steel is eight times heavier than water. Even the natural oil on the fingers, or that obtainable by passing the fingers through the hair, will suffice for the purpose of assisting the needle to float.

The first idea is that the buoyant effect of the oil adhering to the needle prevents it from being drowned. However, the quantity of oil thus attached to the needle is not enough to buoy it; the specific gravity of the oil is, say, 0.9 as compared with water,

[1] From the *Mining and Scientific Press* of July 7 and 14, 1917.

which is the unit of specific gravity; therefore the flotative margin is only one-tenth, and for the oil to float a piece of steel, having a specific gravity of 8, its volume would have to be more than seventy times that of the steel. So the buoyancy of the oil does not do it. Moreover, an ungreased needle also will float. This experiment must be conducted carefully. To be certain that the needle was free from grease [2] I held it in metallic pincers, dipped it in a solution of washing-soda (sodium carbonate, which is a solvent for grease), and then dried it, taking care to use a clean cloth and not to touch it with my fingers. Then I placed a piece of tissue-paper on the water in a cup and laid the needle, held in the pincers, upon the paper, which was depressed gently into the water by the point of a wooden match, until the paper became soggy and finally sank, leaving the needle floating. It lay in a depression of the water-surface, which appeared to be bent under it.

The needle that will float after being greased is larger than the one that floats without being greased,[3] so the oil seems to aid flotation: but when the needle is too large it cannot be made to float, greased or not. It is too heavy; that is, the force of gravity multiplied by mass is sufficient to overcome the peculiar resistance offered by the surface of the water. What causes that resistance?

Surface-Tension. The force responsible for the floating of the needle is called "surface-tension." It is a manifestation of cohesion, which is the attraction that binds molecules of like kind to each other. Each molecule within the interior of the liquid is imagined as surrounded by molecules like itself to which it is attracted and which it attracts equally in every direction, whereas the molecules at the free surface of the liquid are attracted only by those internal to themselves, the result being to constrict the free surface of the liquid. In consequence, the surface acts as if it were a stretched membrane or an elastic film.

[2] New needles are slightly greasy, as I ascertained by means of the camphor test, described later. The grease protects the needles from rusting.

[3] I tried five large greased needles, all of which floated; then I tried the same needles after they had been washed in the soda solution and wiped dry on a clean cloth. One time all five sank; the other time four sank.

These molecular conditions may be represented graphically. See Fig. 1. The attractive forces acting on a molecule (*A*) in the body of the liquid may be represented by four resultant axial components, which are equal, so that the molecule is perfectly free to move, except for viscous resistance. At the sur-

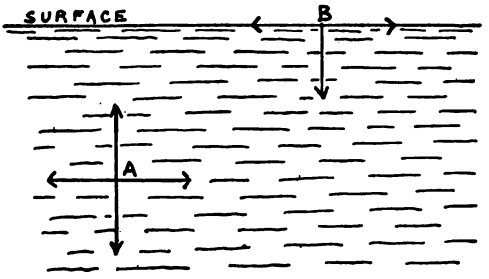


FIG. 1.

face itself the upward component disappears and the pull downward on the molecule (*B*) is uncompensated, any extension of the surface being opposed by a force the horizonal component of which is " surface-tension."

This can be illustrated in another way. Each particle of water is attracted by all the particles that lie within its range,

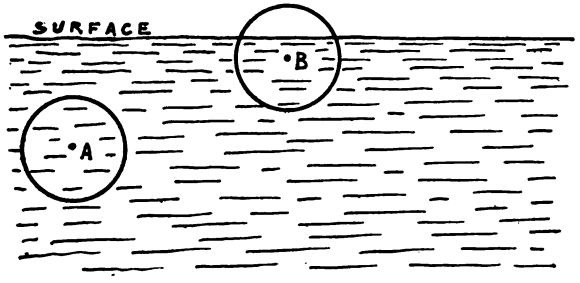


FIG. 2.

which is definitely small, about 0.00000015 cm.; therefore the scope of molecular attraction may be considered as a sphere of influence. Thus *A* in Fig. 2 is attracted, and attracts, within a definite sphere, while *B*, which is close to the surface, is more attracted inward than outward, since a part of its sphere of attraction lies outside the water.

Such a hypothesis is largely an abstraction; a concrete idea of the nature of surface-tension can be obtained by noting some of its various manifestations.

1. The drawing, or "soaking up," of water by a sponge.
2. The penetration of wood by varnish.
3. The rising of oil in a lamp-wick.
4. The clinging of ink to a pen.
5. The running of the ink from the pen to the paper.
6. The absorption of the excess of ink by blotting-paper.
7. The cohesion between two plates that have been wetted.
8. Dip a camel's hair brush in water, remove it from the water, and observe how the hairs cling together. Immerse the brush in the water and note how the hairs separate.
9. Watch the water-spiders running over a pool, like boys skating on thin ice. H. H. Dixon actually measured the pressure exerted by the spider's feet on the water. He photographed the shadow of the dimple, then mounted one of the spider's feet on a delicate balance, and made it press on the water until it made a dimple of the same depth as that previously recorded.
10. Pour colored water in a thin layer over the bottom of a white dish; then touch a part of its surface with a glass rod that has been dipped in alcohol. The colored water shrinks from the part touched, leaving an irregular patch of white bottom dry. This is due to the tension of the pure water being greater than than that of the alcoholized water, so that the liquid is pulled away from the place where the tension is weak to the place where it is strong.[4] The lively movements of the particles of dye in the water indicate the conflict between the forces of diffusion and surface-tension.
11. The formation of a drop at the end of a tube or from the small mouth of a bottle is another example of surface-tension. Note how the drop grows slowly until it has attained a definite size, and then breaks away suddenly. The size of the drop is always the same for the same liquid coming through the same orifice. It hangs as if suspended in an elastic bag that ruptures

[4] This simple experiment is a fascinating exhibition of surface-tension and it should be made by every student of flotation.

when the weight becomes excessive. The contractile character of surface-tension is manifested in the formation of the drop, the force tending to draw the fragment of liquid into the most compact form, that presenting the least surface in relation to volume, namely, a sphere.

Similarly, if we admit air through a glass tube of given size into various liquids, we shall obtain the biggest bubble in the liquid with the highest surface-tension. If various liquids in succession are allowed to run out of an opening of given size, the largest drop will be that of the liquid having the highest surface-tension.

12. When an iron ring is dipped into a solution of soap and then taken out, it will be seen that a film of solution stretches across the ring, covering the whole interior circular space. If a small loop of cotton, previously moistened in the soapy solution, is placed on the film stretched across the circle of the ring, this loop can be made to assume, and to retain, any form, such as is shown at *A* in Fig. 3. If, however, this film within the loop is

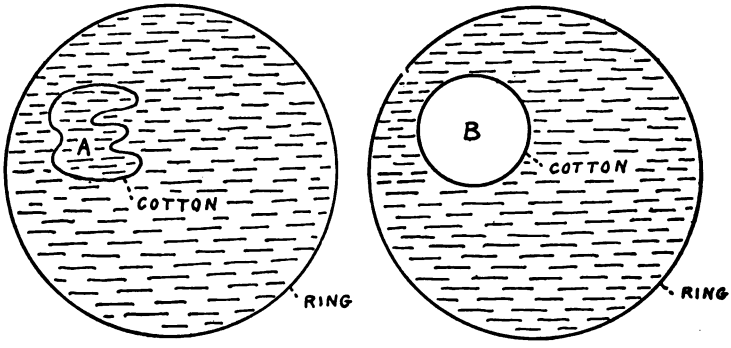


FIG. 3.

broken, the loop immediately assumes the form of a perfect circle, as shown at *B*; and if it is now deformed in any way, it springs back at once to a circle as soon as it is released. Evidently the surface of the solution assumes the shape covering the smallest area. The surface-tension of the liquid acts equally on both sides of the cotton so long as it is wholly immersed, but when the film of liquid inside the loop is broken, the tension acts

on one side only—on the open side, where it is in contact with air —and hence draws the loop into a circle, which involves the minimum of extension.

13. The contractile force of surface-tension is shown in a simple way by blowing a soap-bubble on the large end of a pipe and then holding the other end of the pipe to a candle, whereupon the air escaping from the shrinking bag of the bubble will extinguish the flame, as in Fig. 4.[5]

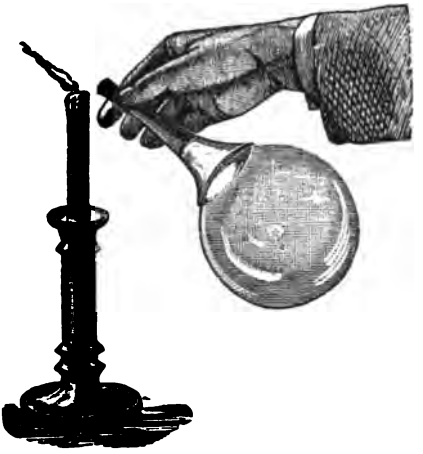


FIG. 4.

14. When water is sprinkled on a dusty floor, the dust prevents the wetting of the floor by obstructing the coalescence of the drops, that is, the spreading of the water over the floor. The water draws itself into rolling spherules that become armored by particles of dust. They are nearly round, the larger ones showing a flattening, because the gravitational stress overcomes the contractibility or sphericity of the film. This flattening is shown by a drop of mercury on glass or by the beads of gold on an assayer's cupel.

15. The globular form assumed by water when spilled on a hot stove is another manifestation of these forces. The water is protected from the hot iron by a film of steam, which, as it is

[5] C. V. Boys in "Soap Bubbles."

formed, decreases the size of the globule until it disappears. If the iron is not sufficiently hot, it becomes cooler and therefore wetted, by spreading of the water, which is instantly converted into steam.

16. Some of the physics of flotation can be illustrated at the dinner-table.

A. Fill a glass a little over-full of water and note the convex surface, indicating the play of a force that prevents the liquid from spilling. It is a contractile force.

B. Fill a wine-glass half-full with port and observe how the wine climbs up the side of the glass, forming a meniscus around the circumference of the surface. This liquid consists of alcohol and water, both of which evaporate, the alcohol faster than the water, so that the surficial layer becomes watery. . In the middle of the glass the surficial layer recovers its strength by diffusion from below, but the film adhering to the glass, being more exposed to the air, loses its alcohol by evaporation more quickly and therefore acquires a surface-tension higher than that of the undiluted wine. It creeps up the side of the glass dragging the strong wine after it, and this continues until the quantity of fluid pulled upward collects into drops—called the " tears of wine "—which run back into the glass.

C. Fill a glass two-thirds full from a " siphon " containing water that is effervescent because it contains gas in solution. Take three or four small grapes, preferably of the Californian seedless variety. The grapes will sink to the bottom of the glass, but soon they become restless and rise to the surface, one after the other. They do not remain there long; first one and then the other sinks. They will continue the performance for half an hour, bobbing up and down. Their activities slowly diminish, and eventually they are left inert at the bottom of the glass. What happens is simple enough. The siphon has come from the refrigerator; the warmth of the room and the lowering of pressure release the carbonic-acid gas, which, in the form of minute bubbles, attaches itself to the grapes, buoying them to the surface as mineral particles are raised to the surface of a pulp in the Potter process. There the bubbles burst, causing the grapes to

fall back. If a couple of grapes collide, the bubbles become detached, dropping their freight, and themselves rising to the surface. At first the grapes rise rapidly and rebound from the surface of the water as if it were an elastic membrane. This is a remarkable effect and should be noted carefully. After the evolution of gas has diminished the bubbles become too few to buoy the grapes, and the performance ends.

Surface-tension is identified with "capillarity," because it is so marked in a tube the bore of which is only large enough to admit a *capillus*, or hair. When the lower end of a wide tube is held in water, the water inside rises to about the same level as that outside the tube, in accordance with the law of hydrostatic pressure; but when the lower end of a glass tube of small bore, say, 1 mm., open at both ends, is inserted into water, the water rises within the tube and stands at a level higher than the water outside. If, again, the tube be held vertically with its lower end immersed in mercury, the liquid metal inside the tube sinks to a level below that of the mercury outside. See Fig. 5. This is

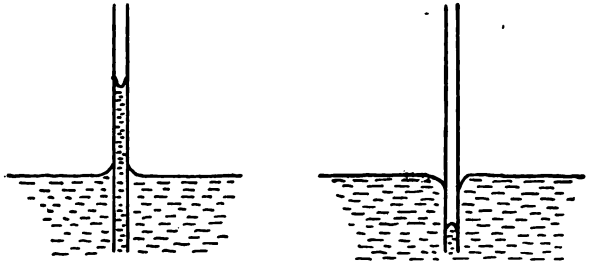


FIG. 5.

Glass Tube in Water. Glass Tube in Mercury.

explained by saying that the molecular attraction of water to glass is greater than that of water to water; whereas the attraction of mercury to glass is less than that of mercury to mercury. The forces of cohesion in a substance and of adhesion between various substances have been measured. Quincke and others have ascertained by experiment that the effect is sensible within a range of one thousandth and one twenty-thousandth of a millimetre. Such is the scope of molecular attraction. The liquid rises in a capillary tube until the weight of the vertical

column between the free surface and the level of the liquid in the tube balances the resultant of the surface-tension.

The surface-tension of liquids can be modified. It is decreased by a rise of temperature. For example, place two matches an inch apart on the surface of pure water in a bowl and then touch the water between them with a hot wire. They draw apart promptly, because the surface-tension of the water between them has been lowered relatively to that of the rest of the liquid in the bowl, so that the pull of the water-surface under normal tension is stronger than that of the surface of the warm water between the matches.

The addition of an impurity or contaminant will lower the surface-tension of water. We have seen how this effect is caused both by alcohol and soap. Distilled water has a maximum surface-tension, which is lowered by almost any substance that is soluble or miscible in it. The soluble substance, or solute, modifies the tension directly, whereas the minutely divisible substance, forming an emulsion, creates a great number of interfaces, or surfaces of contact, each having a lower tension. The particular contaminant, or modifying agent, associated with the early history of flotation was oil, which is partly soluble and rapidly dispersible. The oil generally used at first was a heavy oil, like oleic acid.[6] By the addition of sufficient oil the surface-tension of water is lowered from 73 to 14 dynes per linear centimetre. The following experiment illustrates this fact. If a wooden match be laid on the surface of tap-water in a pan, so that it remains at rest, and if then a drop of olive-oil be placed on the surface of the water near the match, the match will draw away smartly, because the oil has reduced the tension of part of the water-surface and caused the uncontaminated water to pull away. This modification of the surface-tension of water by a contaminant is one of the fundamental factors in flotation, as we shall see.

Let us now go back to the floating needle. If it is greased, does the grease lower the surface-tension of the water? That can be ascertained by a pretty experiment. If camphor is

[6] No wonder the judges were puzzled by the technical terms used in flotation lawsuits. "Oleic acid" is called an oil, whereas "oil of vitriol" is an acid.

whittled with a knife above a bowl of water, the shavings, dropping on the water, will dance on the surface in a life-like manner suggesting insects in a fit. This phenomenon, as shown by Marangoni, is due to the dissolving of the camphor—a crystalline vegetal distillate—preferably at the pointed end, where the largest area per unit of volume is presented for solution. The dissolving of the camphor lowers the surface-tension of the water in contact and thereby causes the uncontaminated water, with its stronger tension, to pull away from the spot affected by the camphor—as in the colored water and alcohol experiment, No. 10. This causes the chips of camphor to turn and move spasmodically. In order to incite such activity the surface-tension of the water must be greater than that of the camphor solution. As soon as enough camphor has dissolved to modify the whole surface of the water in the bowl or cup, the chips become inert. Likewise if the surface-tension be lowered by the addition of grease the camphor remains quiet. For example, if, while the chips of camphor are lively, the water be touched by a greasy finger—all fingers are slightly greasy—the camphor is quieted immediately. No ordinary " clean " cooking-utensil is sufficiently free from grease to allow an exhibition of the camphor dance.

Here we have a simple means of detecting the presence of grease or oil in the water upon which the needle is floating. I introduced some camphor chips into the water on which the ungreased needle was floating and they became lively. Then I repeated the experiment with a needle that was slightly greased, by rubbing it with the fingers that had touched my hair, and the camphor appeared unaffected thereby; it was lively. Finally, I smeared the needle with olive-oil; an iridescence on the surface of the water indicated diffusion of the oil. This time the chips of camphor fell dead as a door-nail and remained wholly inert on the water. Apparently, therefore, the needle will hold to itself a limited proportion of oil, which adheres so selectively as not to contaminate the water; but an excess of oil, more than the needle can hold, will be set free at once to modify the water and lower its surface-tension.

This is a classic experiment, as I ascertained afterward.

Raleigh showed that the decrease of surface-tension begins as soon as the quantity of oil is about half that required to stop the camphor movements, and he suggested that this stage may synchronize with a complete coating of the surface with a single layer of molecules.[7]

A reference has been made already to the measuring of surface-tension. It can be done in several ways. For example, a framework, such as is shown in Fig. 6, is constructed [8] out of a

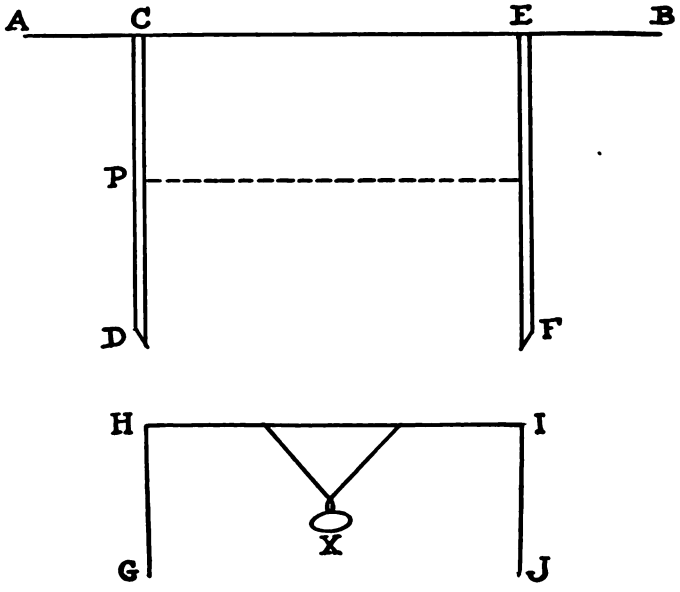


FIG. 6.

transverse bar *AB* and two grooved slips *CD* and *EF*, so as to allow a piece of wire *GHIJ* to slip freely up and down. The wire *HI* is pushed against *AB* and some of the liquid is applied between them. The little pan *X* is loaded with sand so that the wire *HI* is pulled gently from *AB*. The minimum force required to do this is *mg*, the weight of *M* grams. This weight suspended on the film of liquid between *AB* and *HI* equals the ten-

[7] The Encyclopædia Britannica. 11th Edition. Page 267.
[8] Alfred Danniell. "A Text Book of the Principles of Physics."

sion of the film on the wire. If the film stretches until the wire HI is at p, then the film has an area CE, CP. The total weight mg is distributed over the breadth CE, whence if T represents the surficial tension across the unit of length CE, then

$$mg = T \cdot CE, \quad \text{or} \quad T = \frac{mg}{CE}$$

Another simple way of measuring surface-tension is to make a wire-frame of which one side is movable; thus (Fig. 7) let ABC

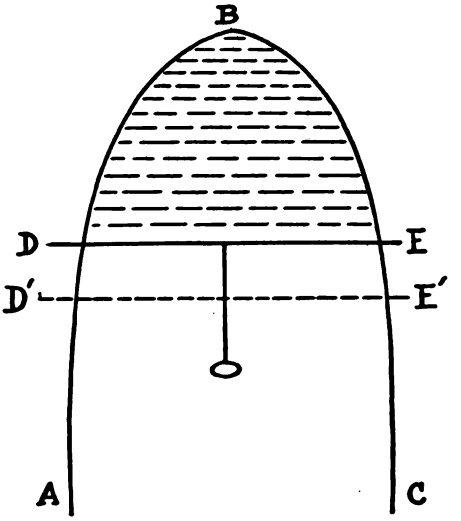


FIG. 7.

represent a bent wire and DE a straight piece. If a film of liquid is spread over the space DBE then the surface-tension acting on DE will support not only the weight of the wire DE but also a small weight X. If W be the mass of the cross-wire DE and its attached weight, then the surface-tension of the film supports W and exerts a force Wg. The surface-tension acts all along that part (l) of the wire DE that lies in contact with the film, and it acts at right angles to DE. Since the film has two surfaces, if the force exerted on a unit length of DE and on one side of the

film be T, then the upward force on DE due to surface-tension is $2Tl$. Hence [9] if there is equilibrium $2Tl = Wg$, or $T = \frac{Wg}{2l}$.

This method was suggested by Clerk Maxwell. An ingenious mechanical model for illustrating the definition of surface-tension has been devised by Frank B. Kenrick, of the University of Toronto. He gives the definition as "the maximum quantity of work that can be gained when a surface is decreased in area by one square centimetre," and describes his device as follows: "A projection cell 40 mm. by 10 mm. and 60 mm. high, the upper edges of which have been coated with a film of paraffine-wax, is filled almost to overflowing with water. On the surface is floated a thin shaving of cork 30 mm. by 5 mm. by 1 mm., to which is attached a fine cotton thread about 40 mm. long terminating in a glass hook. The thread passes over a small pulley made from a pill-box and a pin resting in a double Y-shaped glass bearing. Three weights of glass or bent wire weighing about 0.1 gram, 0.07 gm., and 0.04 gm. may be hung on the hook. The middle weight approximately balances the surface-tension, while the lighter one on being pulled down with a pair of tweezers is lifted again by the surface-tension. A fall of 1 c.c. produces one square centimetre of surface, namely, 0.5 cm.^{2} on the forward under side of the cork that is wet with water and 0.5 cm.^{2} on the upper surface of the liquid in the cell." [10] For the accompanying sketch (Fig. 8) I am indebted to Professor Kenrick, who sent it to me on request. The waxing of the upper edge of the glass cell allows the water, which does not wet paraffine, to rise slightly higher than the level of the glass without overflowing.

By such experiments the force of surface-tension between water and air has been determined to be 3.14 grains per linear inch or 72.62 dynes per centimetre at 20° C.[11] Many disturbing factors enter into the measurement of this force, so that divers

[9] W. Watson. "A Text-book of Physics," page 182.

[10] *Jour. of Phys. Chem.*, Vol. XVI, page 513.

[11] Theodore W. Richards and Leslie B. Coombs. "The Surface-Tension of Water, Alcohols, etc." *Jour. Amer. Chem. Soc.*, July, 1915. One dyne is equal to 1.02 milligrams.

figures, ranging from 70.6 to 81, have been announced at various times.[12]

This force may seem small, yet the actual tensile strength per unit-area of cross-section of the film is about one-fourth that of the iron or mild steel used in the shells of steam-boilers, although its density is not much more than one-eighth as great as that of the iron.[13]

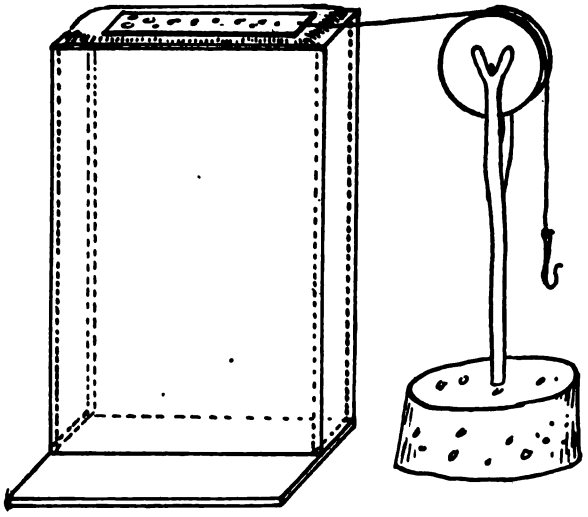


FIG. 8.

The surface-tension of a liquid must be stated with reference to the fluid—gas or liquid—in contact, for it is modified by the nature of the substance on either side of the interface. An interfacial tension exists at any surface separating two substances and it has a particular value for each pair of substances. For example, the tension separating mercury from water is 418 dynes per centimetre whereas that separating olive-oil from air is only 36.9 dynes. A drop of water will not spread over the surface of

[12] T. J. Hoover in his valuable book "Concentrating Ores by Flotation," quotes from Clerk Maxwell's article on "Capillarity" in the Encyclopædia Britannica and gives the figure as 81, but he makes the mistake of saying that it is 81 dynes "per *square* centimetre." It is a tension, not a pressure.

[13] M. M. Garver. *Jour. Phys. Chem.*, Vol. XVI, page 243.

mercury but oil will spread over water. The balance of forces is different in the two cases. When a globule of oil is placed on water, the tension of the water-air surface exerts a pull of 73 dynes as against the joint pull (37 plus 14) of the air-oil and oil-water surfaces. Thus $14+37<73$. (Fig. 9.) The oil spreads. If soap, in the form of $\frac{1}{4}\%$ sodium oleate, be added to the water its surface-tension will be lowered to 26 and the oil-water tension will also be decreased, how much I do not know, but certainly decreased, say, to 12; therefore $37+12>26$, and the oil will not spread over the water. On the other hand, the tension of the mercury-air surface has been given as 436 dynes and that of the mercury-water surface as 418. If this be so, then a drop of water will not spread, because $418+73>436$. But Quincke showed

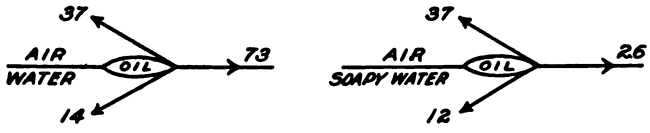


FIG. 9.

long ago that pure water will spread on pure mercury, although the presence of an impurity, such as a slight greasiness, on the surface of the mercury will prevent spreading. According to later determinations of the interfacial tensions, by Freundlich, that of mercury-air is 445 dynes and that of mercury-water 370, so that $73+370<445$, and the pure water ought to spread on the pure mercury, as Quincke stated. If the water be contaminated, so as to lower its surface-tension, it will spread readily even on ordinary mercury, which is not chemically pure and on which pure water will not spread.

Wetting.—A steel needle floats on water, but a glass rod of the same size sinks immediately; yet the specific gravity of steel is to that of glass as 8 to 2.75. The surface of the water resists rupture by the steel but it is readily broken by the glass; in other words, the glass is readily "wetted," while the steel is not. Again, if the glass rod be greased it will float; it ceases to be easily wetted. Here we face one of the underlying phenomena of flota-

tion. The understanding of what constitutes "wetting" is essential to the subject.

If a drop of pure water be placed on a clean piece of glass, it will flatten itself out so as to increase the space it first touched. If a similar drop of water be placed on a cabbage-leaf, it will not spread, but will retain its spherical form. We say that water "wets" a glassy surface and does not "wet" a waxy vegetal surface. A drop of mercury spreads eagerly over gold, but does not spread on glass; mercury wets gold but not glass. The statement is not absolute; it is a question of degree.

If I press the surface of water with a piece of glass the water rises to meet the glass, forming a mound, whereas if I make the same test with a piece of steel the water shrinks away from it, forming a depression. The tendency is for the water to lap the glass but to avoid the steel; the one substance is easily "wetted," the other not. The glass and the steel typify the gangue and the

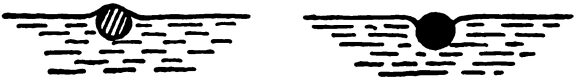


FIG. 10.

sulphide respectively in an ore treated by flotation. If we look carefully at the steel and glass, at the instant of touching the water, we see the conditions sketched in Fig. 10.

Note how ink from a pen will not run on paper that is at all greasy. The paper refuses to be wetted where it is greased. That is why new pens are refractory; the steel has been greased to prevent rusting, like the needles. I used to burn the point of a new pen by aid of a match in order to cause it to deliver the ink to the paper comfortably. That burned the grease, but spoiled the temper of the pen-point.

The free surface of a liquid is horizontal, but at the contact with a solid the surface is curved, the direction and amount of curvature varying as between different liquids and solids. The water curves upward against glass, whereas it curves downward against steel; it tends to drown the one, but to float the other until gravity overmasters surface-tension. The way in which a

liquid impinges on a solid is called the "angle of contact." For example, in Fig. 11 water is shown in contact with glass. Consider the conditions at the point *O*. The gravitational pull on a minute quantity of the water is negligible in comparison with its own cohesive force; so we can disregard the effect of gravity. The force of adhesion exerted by the surface of the glass is represented by *O A*, the force of cohesion in the water is represented by *O B*, and the resultant of these two forces is *O C*. If the adhesive force of the liquid to the solid exceeds the cohesive force of the liquid, the resultant will lie to the left of the vertical, *E D*, that is, within the solid; and since the surface of a liquid assumes

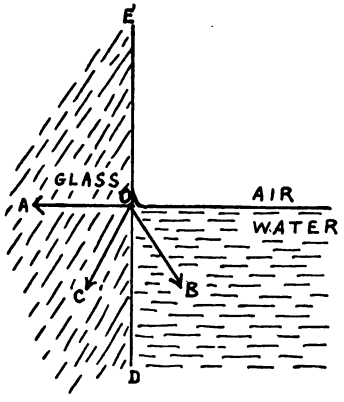


FIG. 11.

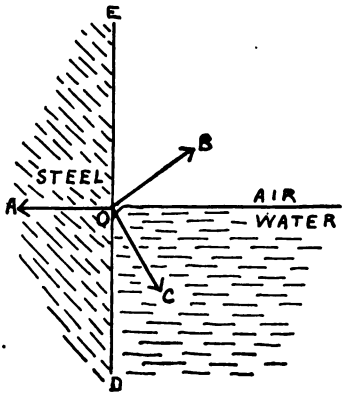


FIG. 12.

a position at right angles to this resultant force, the water rises on the face of the glass. If, on the other hand, as in Fig. 12, where steel is shown in water, the cohesion of the liquid is greater than the adhesion of the liquid to the solid, then the resultant force lies to the right of the vertical, or within the liquid, which accordingly is depressed at the face of the solid.

In Figs. 11 and 12 the contact-angle is *DOB*. Since the surface of the liquid always assumes a position at right angles to the resultant force, the water will tend to rise on the glass and to sink on the steel. This angle of contact between a liquid surface and a solid is usually the same for the same pair of substances,

but there is a subtle variation, which is called "hysteresis" and it is said to play an important part in flotation. The variation is connected with the ability of a solid to condense a film of gas upon its surface. This gas-condensing power, or adsorption, can be modified, by acidulation, for example. Sulman has stated that " whereas the angular hysteresis of silica in plain water may exceed 30°, thus indicating that substance to have a definite power to occlude gas and to float, it drops from 4° to nil in water acidulated with sulphuric acid. Galena, on the other hand, retains its full measure of angular variation, or is but slightly affected."[14] This effect of the surface-energy of solids is apparently an important factor in flotation, and it is a pity that the exigencies of patent litigation have prevented Mr. Sulman from contributing more to the technology of the subject.

The angle of contact between water and glass is so acute as to be more nearly zero the purer the water and the cleaner the glass; between turpentine and glass it is 17°; between mercury and glass it is 148°. In a general way, subject to the variation already noted, the size of the contact-angle measures the capacity for " wetting." This angle can be changed by modifying the surface-tension of the water by means of a contaminant, such as oil, or the angle can be altered by modifying the surface of the solid, also by oiling. The oiling of the steel needle increased the angle of contact with the water so that it did not impinge as directly on the needle, and it did the same to the glass rod, but the effect was relatively less on the steel than on the glass because of the higher specific gravity of the former. The force tending to prevent sinking depends upon the radius of the needle, its density relative to that of the water, the surface-tension of the water, and the cosine of the contact-angle.[15] In metallurgical practice the pull of gravity is decisive in so far as it limits the size of particle that can be floated in water. If our needle is too large, it sinks, no matter how favorable the other conditions may be. So the flotation of a particle of mineral is conditioned on the size to

[14] H. L. Sulman. Presidential address. Trans. I. M. & M., Vol. XX.

[15] Joel H. Hildebrand. "Principles Underlying Flotation." *M. & S. P.*, July 29, 1916.

which it has been reduced by crushing in the mill. The oiling of the needle increased the upward component of the surface-tension by enlarging the angle of contact, but the use of an excess of oil, that is, more than the needle could hold of itself, served to lower the surface-tension of the water and therefore to diminish the resultant force operating against wetting and in favor of flotation. Thus the oil used in flotation has two possible functions, and they may interfere with each other.

If to the water in which a needle is floating I add a drop of pine-oil, the needle sinks at once because the lowering of the surface-tension enables the water to wet the needle, that is, to diminish the angle of contact so that the water envelopes the steel. Let us make some other simple experiments. Take a piece of chalcocite that presents a smooth surface. A drop of water will not spread over it as it will on glass; the globule of water flattens itself on the glass but tends to retain its spherical form on the chalcocite. The glass may typify quartz or some other gangue-mineral. A drop of flotation-oil, such as coal-tar creosote, flattens on the chalcocite, whereas water maintains its sphericity. Coal-tar spreads less on glass than on water, but water spreads more on glass than on chalcocite. Thus water wets mineral less easily than gangue, whereas oil coats mineral more readily than gangue. So we say that gangue has a greater affinity for water than mineral, which, on the contrary, has a greater affinity for oil.

Water drips off oiled copper more quickly than off the unoiled; there is more adhesion between the water and the unoiled metal; the oil prevents wetting by the water. The effect of the density of the surrounding medium is shown by placing a piece of glass under water, dropping a globule of coal-tar upon the glass, and then raising it out of the water. The globule of oil spreads when lifted out of the denser medium and shrinks when returned to the water, although not quite to its first shape, on account of the adhesive surface. The oil on the galena replaces the water on its surface, but the oil on the quartz is unable to prevent the water from pushing itself underneath and over the surface of the quartz. Thus we have " an instance of the selective action of

oil on a metallic sulphide in the presence of water, and the selective action of water on a gangue-mineral in the presence of oil." [16] On this phenomenon largely depends the process for separating valuable mineral from worthless gangue by flotation.

If a piece of galena and a piece of quartz are placed under water on the bottom of a beaker and if a few drops of oil, such as wood-creosote, are dropped upon the water, they will descend through the water owing " to their momentum and the releasing of the surface-tension of the water " [17] until one may fall on the galena, on which the oil will spread, while another falls on the quartz, on which it tends to draw into globular form, instead of spreading. Flotation is essentially a selective process. If I throw powdered ore on water, the particles of gangue sink and the particles of mineral float, in accord with our expectation, based on the foregoing experiments and the deductions therefrom, but some of the small particles of gangue will float and some of the larger particles of mineral will sink, because the play of forces is so complex that any single one of them is not uniformly decisive. Flotation is preferential, not absolute.

Bubbles.—We saw how the floating of the needle was aided by bubbles of air attached to it. That suggests, but does not explain, the latest and most successful phase of flotation. To understand it we must go back to the small boy's soap-bubble. The man who understands the physics of a soap-bubble has mastered the chief mystery of flotation. The boy, who, as pictured by Millais, watches the birth, ascent, and disappearance of the iridescent sphere of his own making, is the type of our modern metallurgist, who makes the multitudinous bubbles constituting a froth and then wonders to what natural laws his filmy product owes its existence.

To put it briefly, the boy, having dissolved soap in water, holds a little of the liquid in the bowl of his clay pipe while he blows through the stem. The soapy water forms a film that is distended by the boy's warm breath into a lovely sphere, which is lighter than the surrounding air, and therefore rises, while the

[16] A. F. Taggart, as witness in the recent trial, at Butte.
[17] Taggart, *op. cit.*

sunlight falling upon it undergoes refraction into the colors of the spectrum. When the boy blows through his pipe into pure water, he makes bubbles likewise, but they burst instantly. The high tension shatters them. They do not burst explosively by expansion of the air within their envelope, but by lateral displacement of the substance composing their incompletely elastic films. To prevent such immediate collapse it is necessary to lessen the tension, that is, to diminish the contractile force at work in the watery substance constituting the exterior of the bubble. This can be done by introducing an impurity or contaminant. Water has the highest surface-tension of any common liquid, so that the addition of almost any other liquid—such as oil, alcohol, or acid—will lower the tension. The boy rubs the soap between his wet hands and dissolves it in the water. The soluble soaps contain an alkaline base, such as potash or soda, combined with a fatty acid, such as oleic or palmitic, extracted from tallow or oil. The boy uses oleate of soda, a compound of soda and oleic acid. The flotationist uses oleic acid, and much of the early work was done with this thick oil. In both cases, boy or man, playing at bubbles or working at metallurgy, the oil serves to lower the surface-tension of the water and to prolong the life of the bubbles that are made out of this modified water.

Two phases of the subject may be compared: The needle that floats on tap-water will sink in distilled water, because the latter lacks the air-bubbles that assist flotation. Although the tap-water has a lower surface-tension on account of its slight impurity, that effect is less decisive than the aeration. The bubble blown in pure water will break almost as soon as it comes into existence, but the solution of a little soap in the water will enable a boy to blow bubbles that sail away beautifully. The lowering of the surface-tension by the contaminant lessens the tendency of the bubbles to collapse. We have seen, in the camphor experiment, how the oil would lower the surface-tension not only of the bubble-film but also of the water in which it might be generated; that lowering of the surface-tension promotes wetting which is antithetic to floating. If to water on which mineral particles are floating, an addition of alcohol or caustic

soda be made, or even the vapor of alcohol be allowed to play over the surface of the water, the mineral particles sink. The intense local contamination of the water has decreased its surface-tension so much as to increase the relative effect of gravity. Instant wetting ensues. It is evident therefore that oil can be used effectively in flotation in two ways: Either in such large quantity as to raise the mineral by sheer buoyancy or in such small quantity as to coat the particles of mineral, in preference to the gangue, and also decrease the surface-tension of the water in such a way as to promote the formation of a stable froth. Luckily the increased wetting power of the water due to the solution or emulsification of the oil is rendered largely ineffective by the oiling of the mineral particles themselves, on the surfaces of which the oil displaces the water and thus prevents wetting, while the lack of adhesion between oil and gangue serves differentially to aid the wetting of the latter by the water.

The changing colors of the bubble indicate that the thickness of the film is not constant; on the contrary, it may vary within wide limits without noteworthy variation of the surface-tension. That makes an important difference between a liquid film and any ordinary elastic membrane. "The tension in a liquid film is independent of the stretching, provided that it is not so great as to reduce the thickness of the film below about five millionths of a centimetre."[18] This result is promoted by the use of a solute that will be strongly adsorbed at the surface of the solution.[19] As the film is being stretched, the new surface formed at the thinner portion will contain less solute, owing to the time needed for adsorption, so that the new surface will be stronger than the old. Likewise, when water has been modified by a relatively insoluble contaminant, the components of the film can so dispose themselves that the surficial forces will be the same everywhere, that is, they tend to remain in equilibrium, including the force of gravity, which otherwise would pull them apart. Thus the tension at the surface of a contaminated liquid

[18] Poynting & Thompson, *op. cit.*, page 137.

[19] Hildebrand. Fig. 2, page 169, *M. & S. P.*, July 29, 1916. Also Willard Gibbs, "Thermodynamics," page 313.

is able to adjust itself within fairly wide limits, and a film made of such a liquid can remain in equilibrium, whereas a film of pure liquid breaks at once. A soap-bubble will last for hours, a pure-water bubble survives for the fraction of a second. Moreover, the presence of a contaminant in water may also affect its viscosity, or internal friction, whereby it offers resistance to change of shape. This strengthens the film of a bubble generated in modified water. It has been asserted [20] that a concentration of the contaminant occurs at the surface of such a liquid, causing the viscosity to be magnified as compared with the body of the liquid. This statement is well founded.

An interesting experiment [21] to illustrate this phase of the subject can be made by floating kerosene over blue-colored water and then passing air into the lower liquid. When bubbles are formed in the oil they are short-lived, but they last long enough to indicate that the oil is not a pure and perfectly homogeneous liquid. In such a liquid, the bubble would break on arrival at the surface. The fact that two bubbles touch without coalescing (*K*, *K*, Fig. 13) proves that there is a film of variable composition between them. When I blow air gently into the colored water,[22] the bubbles that rise into the oil are colorless. They accumulate at the upper surface of the oil, where they show an attraction for each other and also for the sides of the glass vessel. They last longer than the bubbles blown in oil because they are made out of a liquid containing a decided contaminant, the dye. Next, I blow air more energetically, and I note that when the bubble is about to escape from the blue water it raises the surface into a mound (*A* in Fig. 13), emerging at the point of it (as at *B*) as if the air had dragged the water in an effort to overcome a viscous

[20] Samuel S. Sadtler, in Minerals Separation v. Miami suit, 1915. Emphasized recently in the Butte & Superior case.

[21] How variously it can be seen and interpreted is shown by the descriptions given by Messrs. Durell, Norris, and Rickard, in "The Flotation Process," pp. 137, 315, 358; also by Messrs. Taggart and Beach in Trans. A. I. M. E., September, 1916.

[22] Some of these experiments may seem almost childish to the supercilious, but I can commend them not only as giving insight into fundamental principles but as likely to stimulate thoughtful discussion.

layer. This indeed is the fact. I caught one bubble in the act; it came slowly through the little heap of water and remained poised at the top of the mound, finally breaking away, while the water subsided sluggishly to its level. Finally, I introduced air more rapidly into the water. The bubbles broke through the viscous water-oil interface and carried portions of water with them. These portions slipped from the north (*B*, *B*) to the south

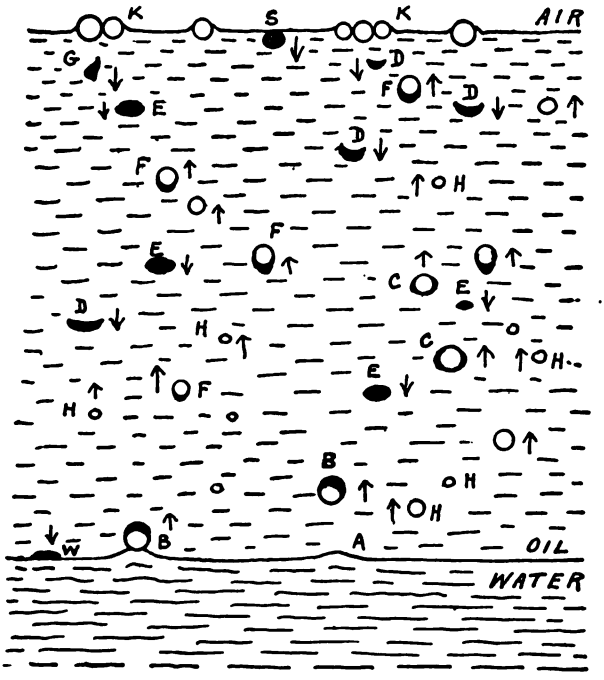


FIG. 13.

pole (*F*, *F*) of the bubbles and fell away, sometimes not until the bubbles had reached the upper surface of the oil. An intermediate stage is shown by *C*, *C*. This water that detached itself from the air-bubble was not a stable film but a viscous coating. It assumed various forms, crescent, hemispherical (*D*, *D*), lenticular, flatly globular (*E*, *E*), or even shapeless (*G*). The retention of a form that is not spherical is proof that the force of surface-tension is overcome by the high viscosity of the film at the

and you find yourself surrounded by a mist that is traveling at the rate of 20 or 30 miles per hour, or even faster; yet as seen from the valley the cloud seems fixed. The explanation is that the moisture-laden air sweeps into the cold area on one side, either the snowy or shady side of the peak, and there the moisture is condensed to globules of water constituting a fog or mist; these are visibly driven forward, to be expanded suddenly and dissipated into clear air as soon as they pass beyond the cold area, but their place is taken by others coming on behind, so the shape of the cloud persists although the substance of it is rushing forward at the speed of a railway-train.

Now the important question arises: What is the substance of the film of the bubble as it passes from one liquid into another? The attachment of blue water to the bubble in the water-oil experiment is confusing, because it obscures the fact that, as the coating of water slips away, the bubble acquires an oily film and when temporarily at rest on the surface it is enveloped in an oily film. No blue tinge can be detected, if the effect of reflection from below be avoided. On the other hand, if the experiment be repeated with heavy oil (colored by "oil orange") and alcohol, it will be found that the bubbles that come to roost at the upper surface of the alcohol are orange-colored. Thus, as scientific theory would suggest, the bubbles take a film of the liquid having the lower surface-tension or less molecular cohesion. In passing from water to oil or from oil to alcohol the bubble has an oily film at the end of its journey. If a bubble were generated in water and passed successively through oil and alcohol, it would have a water, oil, and alcohol film in sequence. If the bubble passed in the reverse direction it would have an alcoholic film in the alcohol, the oil, and the water alike, because alcohol spreads over oil and oil spreads over water, the liquid having the less cohesion or surface-tension being pulled by the molecular attraction of the liquid having the stronger cohesion or surface-tension. There is this to be added, however, that the bubble generated in water would have some water in its oily film when in the oil, and some oil in its alcoholic film when in the alcohol. Each liquid in turn serves slightly to contaminate. On the return journey, the

alcoholic film, contaminated slightly by the air and by any impurity in the alcohol-air interface, would resist modification by the oil and by the water (forming the lower layers of liquid) because the alcohol would spread over both the oil-air interface and the water-air interface. Imagine a globule of oil in an air-bubble enclosed by water (Fig. 15): the oil spreads and forms a film to enclose the air. Now imagine a globule of water in an air-bubble surrounded by oil; the water does not spread, because the pull of the air-water and water-oil surfaces is greater than that of the oil-air surface; therefore a water-filmed bubble will acquire an oil film when passing into oil; on the other hand an oil-filmed bubble will retain its film in making the same entry through water.

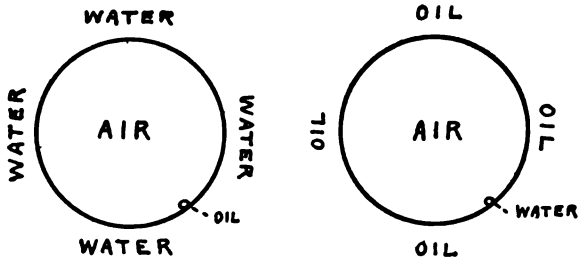


FIG. 15.

We have seen that mineral has a selective adsorption for oil rather than for water and that in this respect it differs from gangue. Metallic particles adsorb air, but this fact is relatively unimportant in flotation because the air approaches them when it is enclosed within a liquid envelope that is contaminated by oil. Therefore the adhesion of oil for the metallic surface becomes the dominant factor. The older notion that the affinity of air for metallic surfaces played an important part in flotation has been set aside, because of the absence in the flotation-cell of any direct contact between air and mineral. Metallic surfaces, such as those of minerals, are supposed to adsorb air and that is why they are not readily wetted. It may be due to molecular density, coupled with reduction of inter-molecular distance, which is practically the same thing as a reduction of sub-capillary

porosity. Adsorption of air would also bear a relation to the higher density of the mineral. Such adsorption plays its part in the older surface-tension processes, such as those of Wood and Macquisten, but in the later flotation processes there is present insoluble oil or a soluble frothing-agent, and this renders it impossible for the globule of air to come into direct contact with the mineral. It is not the air, but the film around it, that provokes the attachment of the bubble to the mineral.

Now let us consider the air-bubble made in water containing an impurity that decreases its surface-tension. In the language of flotation we would say that this impurity is a contaminant modifying the water. As soon as the air enters the water it assumes a globular form as before, but when the bubble reaches the surface it persists; it does not burst at once. The bubble in the water is a spherical hole occupied by air; the air has displaced the water and is enclosed by it; the water-surface in contact with the air is in a state of tension as compared with the interior body of water, and that causes contraction into spherical shape. The surface-tension has been lowered by the contaminant so that the bubble-film is in a state of less strain than a similar film of pure liquid, hence a diminution in the tendency to contract and to collapse. Moreover there is a tendency for the contaminant, whatever it be, to concentrate at the air-water surface; there is a differentiation of the constituents of the liquid, causing the surface to differ slightly in composition from the bulk of the solution and so to accentuate the modification due to the presence of the impurity. The bubble-film or air-liquid contact adsorbs the contaminant until equilibrium is established, and the contaminated liquid of the film carries some of the contaminant all the way to the surface, despite the interchange between molecules or particles of the contaminant on the way up. This differentiation and concentration of the contaminant at the surface of the water in contact with the air-bubble may indeed be likened to a film or membrane, so that the bubble may be regarded as a sac, but it is a sac the substance of which is not fixed while the bubble is moving upward through the water. It cannot be regarded as enclosed within a definite film until it reaches the end

of its journey, and even then the film is coterminous with the surface at which it rests, and the play of light upon it shows that the rearrangement of its substance is still in progress, as the excess of liquid drains to the south pole. The variability in the surface-tension due to the shifting of the contaminating particles is essential to the longevity of the bubble-film. That brings us to a recognition of an important factor: viscosity.

Viscosity.—This is defined as the internal friction of a liquid or its resistance to a change of shape. Two years ago the part played by viscosity in establishing a bubble-film was subordinated to emphasis on the lowering of the surface-tension of the water in the ore-pulp.[24] Since then this branch of the theory has been elucidated by Messrs. Taggart, Beach, and Bancroft.[25]

The addition of alcohol increases the viscosity of water up to about 47%, after which the further addition decreases the viscosity. Alcohol, of course, lowers the surface-tension of water, but an experiment [26] will prove that the change of viscosity is the dominant factor in making a froth. If alcohol, to which 5% water has been added, be stirred violently in the glass-jar machine familiar to flotationists there will be no formation of froth, but if the experiment be repeated with tap-water, to which 1% of alcohol is added, then a froth is produced at once.

Such an alcohol-water froth is non-persistent, because the absolute viscosity is low. To increase it we must have a colloidal suspension; for example, the foam on beer. The colloidal protein of beer yields a froth that lasts longer than the bubbles on champagne, which are short-lived, like the alcohol-water foam of the experiment just described. To obtain a froth sufficiently persistent to serve a metallurgic purpose it is necessary to increase the viscosity of the bubble-films. This is one of the functions of the oil, and it is one that follows upon its affinity for

[24] However, I pointed to the probability of viscosity contributing to the tenacity of the film, even in the needle experiment on tap-water, and quoted Boys to show that increase of viscosity was involved in the lowering of surface-tension in enabling a bubble to persist. *M. & S. P.*, September 11, 1915, p. 385.

[25] More particularly in their expert testimony at Butte, from which I have quoted already.

[26] Described by Wilder D. Bancroft in his testimony at Butte.

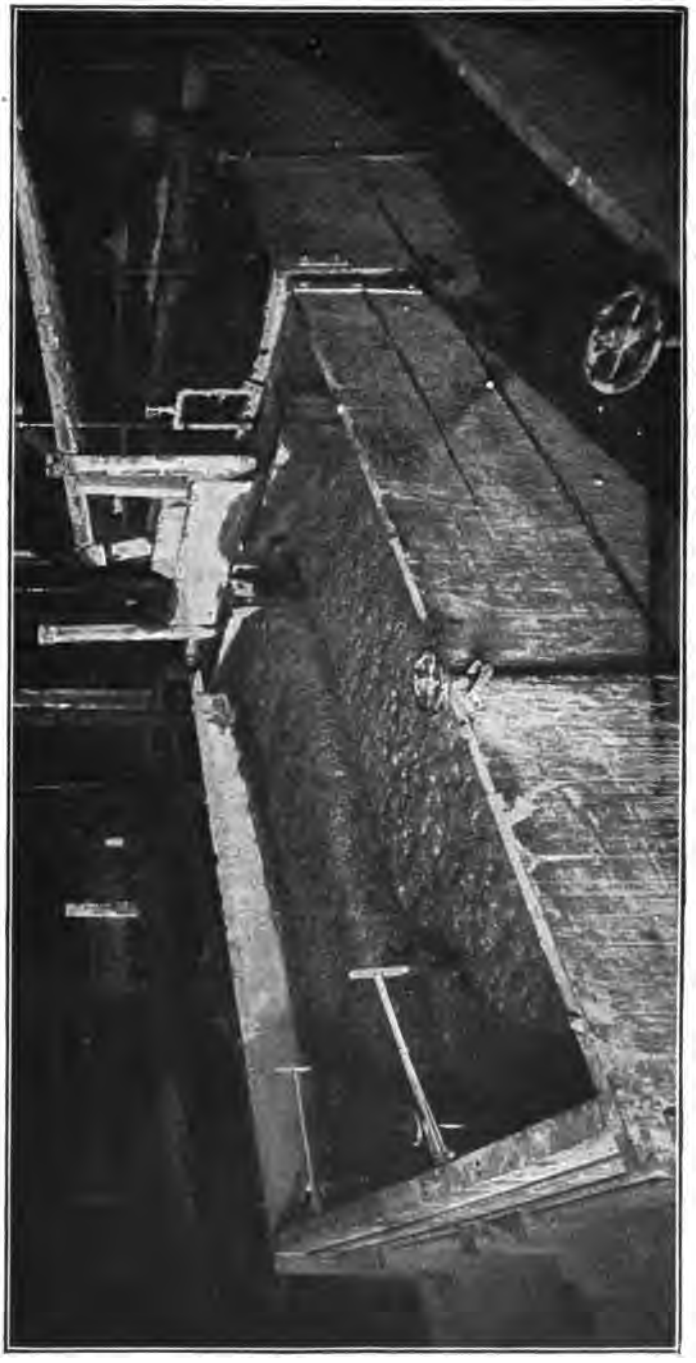


FIG. 16.—The Froth in a Callow Cell.

metallic surfaces. It adsorbs or concentrates (at the surface of the bubbles) the mineral particles in the pulp so as to form an interface that is more viscous than either the oil or the water or the mixture of the two.[27] It is the presence of solid matter that contributes to the viscosity of the bubble-films in the froth.

If a needle be floated on water by means of a raft made of wooden matches and if a chip of wood be floated to one side of it, one can use a magnet to turn the raft and needle on the surface of the water without moving the chip. This shows that the surface, or water-air interface, has no noticeable viscosity.[28] If, however, the surface be dusted with finely pulverized ore, then the magnet will cause the chip to move with the rafted needle. The viscosity has been so greatly increased by the addition of solid matter to the interfacial film that the surface behaves as if it were solid. Next, if a drop of oil, sufficient to lower its surface-tension, be added to the water, the chip will not turn when the rafted needle is moved by the attraction of the magnet. Such increase of viscosity as has been caused by the oil is insufficient to form a resisting medium. Finally, if powdered ore is dusted upon the oil-contaminated surface, again the chip does not move with the raft, because " the surface has been stabilized and made highly viscous."[29]

If water and kerosene be poured successively into a glass bottle, and if then finely-divided copper, called " bronze powder," be introduced and the contents of the bottle be subjected to vigorous shaking, and then allowed to remain quiescent, the copper powder collects at the oil-water interface and from it slowly a bronze film will separate itself and become pendant. This, when viewed by transmitted light, is seen to be a lace-like fabric, like a cobweb that has been long exposed to dust.[30] It is a film of

[27] Taggart.

[28] Taggart. He pointed to the fact that the addition of the oil increased the viscosity of the surface so as to cause it to act as a solid within small distances, close to the raft, but considerably less than when the powdered ore was sprinkled upon the oiled surface.

[29] I am quoting from Mr. Taggart's testimony, from which the description of the experiment also is taken.

[30] F. E. Beach, who performed the experiment in the court-room at Butte. R. B. Yerxa repeated it for me at Miami.

FIG. 17.—Another Photograph, showing the Froth of Two Adjacent Cells.

particles of kerosene and water so viscous, owing to the inclusion of the powdered copper, that it hangs like a curtain; it is an adsorption layer of bubble-film matter hanging from the oil-water interface. The presence of the powdered copper has stabilized the film.

It is important to note that such increase of viscosity as prolongs the life of the bubble-film need not be metallic. When pine-oil is added to water, and the mixture is agitated, the froth that comes to the surface of the water is thin and evanescent. When to this there is added lycopodium powder, which is of vegetal origin, being the spores of club-moss, the froth becomes thick and lasting.[31] If the lycopodium be used without the pine-oil, no persistent froth is made. In this case, as with the bronze powder, the effect of the solid is to stabilize the froth by making the bubble-films more viscous. The gangue would serve for this purpose if the particles of gangue could pass into the oil-water interface, but it happens, as we have seen, that the oil exhibits a choice for the particles of mineral, so that they are adsorbed preferentially.

Another experiment:[32] When a needle was floated on water in a beaker and a drop of castor-oil was added, the needle did not sink. When another drop of the same oil was added, the globule moved to the needle and adhered to it. But it continued to float. When a drop of pine-oil was allowed to run down the side of the beaker, the needle sank as soon as the pine-oil touched the water, while the globule of oil remained afloat. Apparently the increase of viscosity due to the thick oil counteracted the lowering of the water's surface-tension.

The effect of saponine, noted in Hoover's book as being so detrimental to flotation, can now be explained. Although it does not increase the surface-tension of water, but tends rather to decrease it very slightly, according to Freundlich, it causes a marked increase of viscosity. The result is a good froth; but it exhibits no essential adhesion, that is, the saponine solution is

[31] Bancroft, who performed the experiment in the court-room at Butte.

[32] Made for me by Mr. Yerxa in the laboratory at Miami.

not adsorbed by the mineral. Therefore the froth does not persist and the mineral is not floated.

Any substance that is adsorbed into the oil, or the oil-water interface, of the bubble will pass into the film. If it does that the substance will be floated. Mineral goes into oil in preference to gangue. If a particle of sulphide is in the vicinity of oil and water, the oil-surface of the sulphide grows larger and the water-surface grows smaller, until the sulphide at the last takes a position within the oil. Reversely, a particle of quartz takes a position within the water. The greatest possible area of sulphide that can be covered by the oil is when the sulphide is within

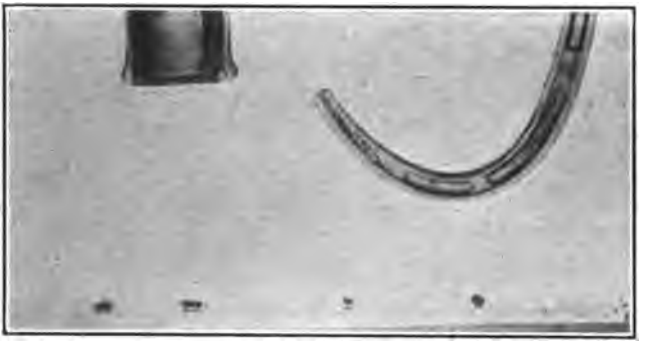
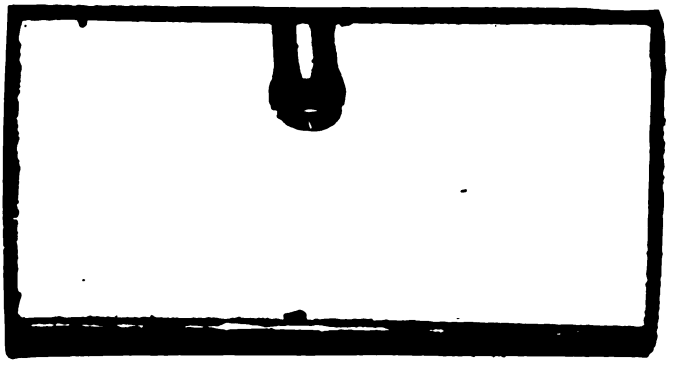


FIG. 18.

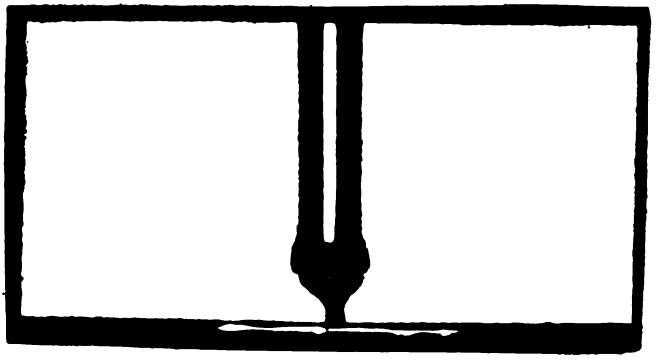
the oil; therefore the particles of sulphide tend to encase themselves within the oily substance of the bubble-film and so not only stabilize it but give themselves the opportunity of being floated to the surface in the froth.

Oil-Films.—In the course of the first trial of the Miami lawsuit, at Wilmington, a series of demonstrations was made in court for the purpose of argument. These experiments were photographed and placed in the record. Some of them are of scientific interest. Fig. 18 shows the curved pipette employed to pass an air-bubble to the bubble-holder, which is a bell-mouthed glass tube. Fig. 19 shows the play of a bubble on the oil placed upon a particle of galena lying at the bottom of a vessel containing water. In *A* the particle of galena and the bubble-holder are



A

B

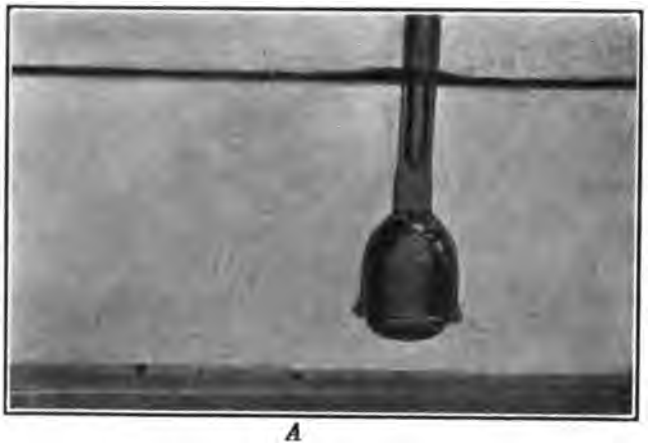


C

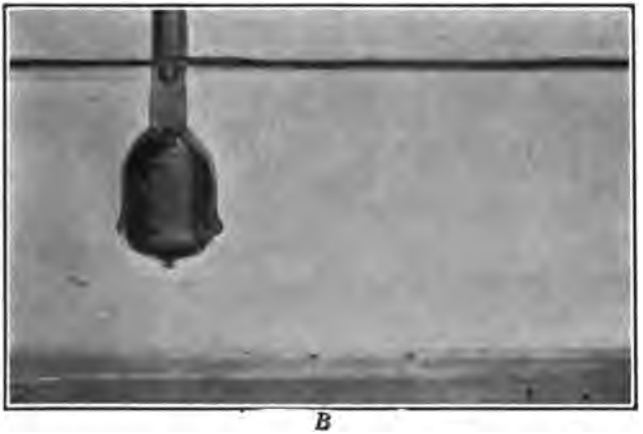
FIG. 19.

shown. In *B* a globule of oil rests on the galena. The oil is 1½ times the volume of the galena particle. In *C* the air-bubble is adhering to the oil on the galena and drawing it up, forming a neck of oil between the bubble and the galena. The photographs exhibit the affinity of the oil for the air-bubble. If the bubble failed to raise the particle of galena, this should not occasion surprise, as it was much too large—several thousand times bigger than the average particles treated in flotation. In Fig. 20 similar experiments on particles of unoiled galena of a reasonable size—about 20 mesh—are recorded photographically. In the first of this series the bubble-holder is approaching one of three particles, in the second it is moving away with one of them, and in the third with another. In Fig. 21 another series of experiments is shown, but with oiled particles of galena, of plus 20-mesh size. In the third member of this group it will be noted that all the galena particles are being carried away by the bubble. Two of these particles are adhering to the third particle, which is attached directly to the bubble. Ordinary tap-water was used. These experiments, and others like them, showed that particles of galena will adhere to an air-bubble, whether they are oiled or not. The adhesion takes place even when the mineral carries an excess of oil. Particles of chalcocite do not adhere so readily to the air-bubble when they are unoiled as when they are oiled, but the evidence given in this suit was incomplete; moreover, it was not shown whether a bubble made out of water suitably modified will, or will not, adhere to an unoiled particle of chalcocite. The motion-pictures of these demonstrations cost a great deal of money, but it will be acknowledged now, I believe, that they threw but little light on the theory of flotation.

The adhesion of air, as a bubble in water, to mineral particles is easy enough to prove, but such bubbles, as far as I have been able to ascertain by experiments, will adhere to almost anything that happens to be near-by. Trying some of these experiments recently with Mr. Yerxa, at Miami, I found that a large air-bubble would not lift an 8-mesh particle of chalcocite without a good deal of coaxing, but when a minute (accidental) air-bubble became poised on the chalcocite then the big bubble attached



A



B

C

FIG. 20.

A

B

C

FIG. 21.

itself to the small one and thereby raised the mineral particle. When the chalcocite was oiled the particle was lifted without hesitation. Examining the bubble-film, it will be seen (Fig. 22) that the particle of chalcocite hangs from it when in the water, but as soon as the bubble is taken out of the water into the air,

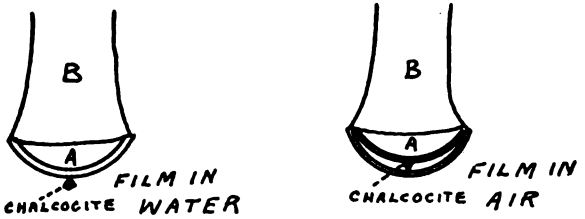


FIG. 22.

the chalcocite is enclosed between an inner and an outer surface,[33] in both of which the oily contaminant is so concentrated as to form an adsorption layer.

The nature of this oil-water interface is indicated by another experiment. If water and pine-oil are poured successively into a test-tube and a particle of chalcocite is dropped into it, we shall

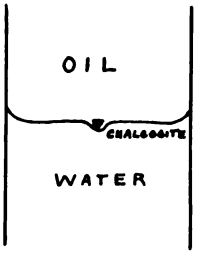


FIG. 23.

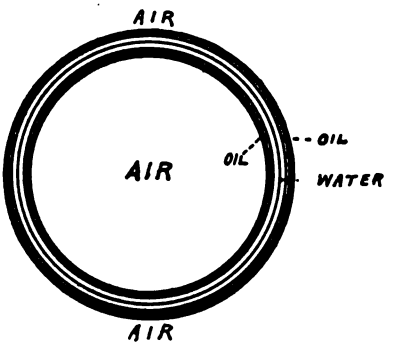


FIG. 24.

find (Fig. 23) the particle floating at the oil-water interface in such a way that the mineral seems to be in the water, when it is really enclosed within a downward protrusion of the oil.

When a bubble is in oily water it has only one contaminated surface, or adsorption layer, but when it emerges it has two. See Fig. 24. The oil is concentrated at the surfaces in contact

[33] As elucidated by Taggart at Butte.

with the air, outside and inside, leaving the less modified water between.

Again, when a globule of pine-oil was placed on the smooth surface of a lump of chalcocite under water, the pine-oil was held by the chalcocite as against a bubble brought in contact with it, but when the globule of oil lay on a piece of quartz the pine-oil was adsorbed by the bubble. A particle of mineral and a bubble show mutual attraction and if the mineral particle is minute it becomes drawn into the interface of the bubble-film. That may be why larger particles are not floated easily; they are too big to be enveloped in this way. The mineral particles are carried within the bubble-film; they are not attached to it outside. That may explain why fine pulverization is essential to the success of flotation. Thus we arrive at the idea that it is not the air in the bubble only, but the nature of the film, that affects the floatability of the metallic particles.

The addition of oil to water—in a beaker, for example—causes an oily film to appear at the interface between water and air. When an air-bubble meets an oil-globule they will be mutually attracted and some of the oil will pass into the interface between water and air. When air occupies a hole in water, forming what is called a bubble, the periphery of this hole presents a surface—exposed to the air within—like the surface of the water in the beaker. In each case the oil tends to concentrate at that air-surface.

The old idea that the mineral particle attached itself directly to air is now relegated to one side; while this mutual attraction may exist, it plays a minor part because the air when it approaches the mineral in a pulp is always enclosed within a watery film contaminated by oil or some substance that functions similarly. This statement has been made previously and is repeated here for emphasis.

It has been disclosed by microscopic examination [34] that the mineral particle is not in direct contact with air, but so enclosed within the film as not to be in touch with air either inside or outside the bubble in a mass of froth. The film raises itself over the

[34] Taggart.

particle and wraps itself under the particle, so that the mineral is enclosed within a watery interspace. The film itself consists of an exterior surface in which the oil is concentrated, and of an interior surface in which oil also is concentrated, both of these oily concentrations grading toward the water that lies between them. The oil is concentrated at each gas-liquid interface, just as oil concentrates at the surface of water in contact with the atmosphere.

The various experiments described in the foregoing pages have shown that the oil in a pulp, consisting of crushed ore and water, performs three distinct functions:

1. It lowers the surface-tension of the water.
2. It assists in the selection of the mineral particles.
3. It promotes the formation of a stable froth.

Water is a convenient liquid for flotation work because it has a surface-tension so high that the addition of almost any other liquid will lower it. The lowering of the surface-tension diminishes the contractile force in water and lengthens the life of the bubbles that are formed by the injection of air; but this lowering of the surface-tension has another important consequence: it creates such a variable concentration of oil in the watery film of the bubble as to enable the film to adjust its strength to external forces. This variability of tension is even more important than the lowering of the surface-tension, because it serves to strengthen the film where necessary by lessening the proportion of contaminant at any weak spot. The contaminant will concentrate at the surface of the liquid because by doing so it will decrease the potential energy.

Next comes the selective adsorption of mineral particles by the oily film. The oil wets mineral in preference to gangue; it envelops the mineral, by which it is "adsorbed" or attracted. This causes the particles of mineral to be drawn into the oily film of the bubbles, which in turn are strengthened by reason of the increase of viscosity imparted to their films by the inclusion of mineral particles. The electro-static hypothesis has been discarded in the latest investigations.

Any substance that will lower the surface-tension of water

and be adsorbed by mineral particles would appear to promote flotation. The value of a flotation-agent depends upon its ability to "adsorb" mineral. Most "frothers" or bubble-makers by themselves are not satisfactory because they lack this ability, and, in order to correct the deficiency, it is customary to add a "non-frothing" oil, which is adsorbed strongly by the mineral, thereby promoting successful flotation.[35] A froth made with a relatively soluble oil, like pine-oil, can be stabilized by adding a relatively insoluble viscous oil, like fuel-oil. The idea of agitation, whether of the violent and mechanical kind or of the gentle and pneumatic kind, is to bring the particles of mineral in contact with the oily films of the air-bubbles. Whether the oil is emulsified before or after it is added to the pulp does not matter at this stage, but the oil must have been presented to the bubbles in a minutely subdivided condition, so that they may acquire oily films and so that those films may come in touch with the mineral particles. In doing so the globules of oil and the bubbles that they contaminate beneficially come in contact with particles of gangue as well as particles of mineral, but owing to the tendency of oil to replace water at the surface of the mineral particles these will be coated with oil and adsorbed into the oily film of the bubbles and rise, whereas, by reason of the tendency of water to displace oil on the surface of gangue-particles, those will become wetted and sink.

"Mineral," "metallic," even "ore," are used interchangeably in the technology of flotation. The misuse of "ore" has caused great confusion, for the object of the process is not to recover the "ore," but only the valuable mineral in the "ore," rejecting the valueless portion, called "gangue." As between "metallic" and "mineral," the reference is not so much to substances containing metals, for that would include much of the gangue, such as rhodonite and feldspar, but particularly to minerals having a metallic lustre, which feature appears to be favorable to the adhesion alike of air and oil. "Sulphide" is another synonym, because the sulphur compounds with the base metals are particularly the object of flotation, but "sulphide" would exclude the

[35] Bancroft. In his testimony at Butte.

tellurides. At least one sulphide without metallic lustre is amenable to flotation, namely, cinnabar. So is graphite, which is neither sulphidic nor metallic, except in lustre. Likewise certain forms of scheelite respond to flotation, and it has been shown by experiment that a stable froth can be made with lycopodium powder, which is of vegetal origin. So we must be careful in our use of terms. The use of "metallic" and "mineral" as adjectives to designate floatable substances is based on a concept of flotation that may soon be discarded. No classification of floatable minerals can be made yet, and when it is made it must be based on a better understanding of the physical conditions governing flotation.

The amount of oil required in froth-flotation depends upon three factors: the proportion of mineral to be concentrated, the amount of water, and the degree of aeration. Air and water are needed to make bubbles; these bubbles must be oiled in order that they may engage the mineral in the pulp. The more numerous the mineral particles the greater the number of oily bubbles needed to arrest them. If the amount of water is doubled, there will be only half the number of mineral particles in a unit of space; therefore more oily bubbles will have to be sent in search of them than if they were herded within the smaller volume of water. The idea that a "critical" proportion of oil—somewhere under 1%—is required to perform successful froth-flotation has no basis of evidence outside the imaginings of a group of patentees and it has been stultified by the operations of 1000-ton plants using 22 or 23 pounds of oil per ton of ore, in Utah and Montana. As Wilder D. Bancroft has said: "The hypothesis of a 'critical point' rests on unverified and unverifiable statements."

The Hypothesis.—Let us recall the principal points in the evidence before venturing upon a summary of our conclusions. I write in the plural advisedly, for the evidence has come from many sources and the suggestions explaining it have been borrowed from many writers; the theory, like the practice, of flotation is the joint work of a large number of investigators.

(1) The needle that floats on tap-water will sink in distilled water. Although contaminants have lowered the surface-ten-

sion [36] of the tap-water, it has more sustaining power on account of its aeration.

(2) The bubble blown in distilled water will break as soon as it emerges, but the solution of an oily substance will enable a boy to blow bubbles that sail away beautifully.

(3) The addition of oil lowers the surface-tension and thereby promotes wetting, but the adhesion of the oil to the surface of the mineral particles causes the water to be displaced, so that the gangue preferably, not the mineral, is wetted, and drowned.

(4) Emulsification of the oil provides a means, through the subsequent breaking of the emulsion, for imparting oil in a minutely subdivided state, as needed, for oiling the bubble-films and the mineral particles.

(5) The contaminant, such as oil, in water concentrates at the air-surface and by doing so affords a surface-tension sufficiently variable to be adjustable to shock.

(6) The oil-water interface is more viscous than the body of either liquid.

(7) Oil is attracted and adsorbed by mineral particles, which therefore are pulled into the oily film of the bubbles.

(8) Bubbles will break when they collide unless there is a stable film between them, preventing coalescence. Such stability is furnished by a dissolved substance that adjusts the surface-tension and also increases the viscosity of the film.

(9) A multiplicity of bubbles, or " froth," will serve a metallurgic purpose if it floats valuable mineral matter long enough to facilitate a separation from the valueless components of the pulp.

The recent trend of hypothesis—it has hardly the status of a theory—is to subordinate sundry ideas prominent a year ago.[37] The direct " adhesion " of air to mineral particles is not so vital as was supposed, because air and mineral rarely come in direct contact in the flotation process; usually either the air-bubble has an oily film or the mineral itself has undergone oil-filming. The

[36] The layer of liquid subject to surface-tension has a thickness less than the radius of molecular action. R. S. Willows and E. Hatschek. "Surface Energy," page 8.

[37] "The Flotation Process," 1916.

lowering of the surface-tension of water is still a fundamental factor, but this modification of the water is recognized as chiefly important not for the first consequence, which promotes the wetting of the mineral, but for its secondary result, which is to create a variable tension on the surface of a bubble-film, and thereby strengthen it greatly. The addition of acid has ceased to be essential, it having been found that alkaline water is better for the treatment of many ores. The acid, like the oil, is supposed to serve more than one purpose:

(1) To adsorb on the gangue and aid the wetting of it.

(2) To promote the flocculation of gangue-particles and the separation of them from the valuable mineral.

Fine grinding of the ore is recognized as necessary, not only to separate the mineral from the gangue, but to assist the making of a froth rich in mineral. No longer is the mineral supposed to be buoyed by the bubbles, as if tied to a cork, but the minute particles of mineral are believed to be drawn into the bubble-film, so that, to pursue the simile, the life-preserver of cork surrounds and encases the thing to be floated. The idea that a fixed proportion of oil to "ore" is necessary has gone with the supposition that "oil" only will perform the absorptive function necessary to a stable froth. Colloidal sulphur, sulphur di-oxide, and salt-cake have been proved effective agents in froth-flotation; and we may expect a steady increase in the discovery of such substances until oil, which is expensive, is discarded. The parts played by emulsification and by the formation of colloid hydrates are becoming recognized as possibly important factors. The violent type of agitation has been found unnecessary, and, thanks to recent litigation,[38] it is likely that the use of compressed air under low pressure will supplant the power-consuming devices of an earlier period. The trend is toward simplicity both of treatment and apparatus. When air and a cheap modifying agent are found adequate for the making of a mineral-bearing froth, the flotation process may be deemed fully developed.

[38] See chapter on "Litigation" elsewhere in this volume.

THE FLOTATION OF GOLD AND SILVER MINERAL[1]

By T. A. RICKARD

IN the title to this article I have avoided the use of the word "ore," because the object of flotation is to float not the "ore" but the valuable mineral in the ore, leaving the gangue to sink. It is a selective process, based upon the idea that the ore consists of valuable and of valueless components, which must be separated so that the valuable component may be concentrated as cleanly as possible previously to a final treatment in which the metal or metals are extracted and prepared for the market.

Some of the earliest work in flotation, such as that at the Glasdir mine, in 1896–1899, was done on an ore containing gold and silver, but the recovery of the precious metals was incidental to the concentration of the chalcopyrite with which they were intimately associated. Likewise the saving of the silver in the Broken Hill ore was incidental to the recovery of the sulphides of lead and zinc. In such cases—and they are typical—the floatability of gold and silver in the native state, or of their mineral compounds, does not present any special problem because the recovery of the gold and silver follows the concentration of the base-metal sulphides by which they are usually so closely accompanied in ore deposits. However, the floatability of native gold, as of native silver, hardly needs special demonstration here. "Float gold" has been a bugbear of processes in which water is used, whether in the sluice-box of the gulch or in the stamp-mill on the hillside. Small particles of gold, particularly when flaky, are easily transported on water, as every miner has learned to his sorrow. The platy form of gold, so common in veins, lends itself readily to flotation, if the particles are small, by offering a large

[1] From the *Mining and Scientific Press* of August 25, 1917.

surface to the play of surface-tension and to the adhesion of air. The high metallic lustre of gold is a characteristic that experience in flotation would lead us to associate with easy buoyancy in the presence of air and of oil. If the gold is " rusty," that is, coated with iron oxide or with manganese di-oxide, or, as more rarely happens, with a film of silica, we should not expect it to float, as we should not expect it to amalgamate or to cyanide freely, until it had undergone such abrasion as would expose a fresh clean surface. Similarly gold in a clayey ore may make trouble for any process in which water is used, but this, like the " rustiness," is nothing new and is not peculiar to flotation.

As regards silver, the same general ideas apply. Silver in flaky form is elusive when running water is used, because it is readily floated; likewise when it presents a clean surface it is easily amenable to the guidance of the ascending bubbles. One would expect native silver and those of its compounds that are either highly lustrous, or have a marked cleavage, to float easily. This is a fact. Experiments made at Cobalt [2] showed a recovery of 92 to 97% for metallic silver, 77 to 89% for argentite, 85 to 87% for pyrargyrite, 78 to 80% for proustite, and 69% for friesleben ite. These experimental results have been confirmed in practice, a recovery of 96% having been made by using oil-flotation to supplement gravity-concentration.[3] Of manganiferous silver ores, a type familiar to the Mexican miner, it can be stated that when they cannot be cyanided they also cannot be floated. The obstacle probably is the double oxide of silver and manganese. Even preliminary sulphidization appears ineffective because the sodium sulphide will not attack the manganese-silver compound.

As regards the economic gold minerals, namely, the tellurides, they are so lustrous that one would expect them to be eminently floatable. That would apply to the silver tellurides also. Such has been the experience at Cripple Creek, provided, of course,

[2] Canadian Mining Institute. Bull. No. 62. J. M. Callow and E. B. Thornhill.

[3] At Cobalt the flotation cell has replaced the slime-table in the McKinley-Darragh mill, while in the Nipissing, Buffalo Mines, and Dominion Reduction mills the cyanidation of tailing has given way to re-grinding and flotation.

that oxidized ore is carefully excluded from the mill-feed. At the Vindicator mine the practice is to wash the oxidized material out of the ore before it goes to the flotation plant. At the mines on the Mother Lode, in California, where the carbonaceous slate causes trouble by re-precipitation of gold in the cyanide solution, it has been found advantageous to apply flotation after amalgamation.

However, even if sundry gold and silver minerals will float, that does not mean that they can be recovered successfully as a concentrate by the frothing process. Direct floatability would refer to the surface-tension methods, such as those of Wood and Macquisten.

For the success of the older methods, such as that introduced by the Minerals Separation company, employing mechanical agitation, it is necessary that the pulp should contain finely divided mineral able to pass into the oil-water interface and in quantity sufficient to stabilize the air-bubbles by armoring them. Thus, a clean gold-bearing quartz is unsuitable to a machine working on the principle of violent agitation unless, of course, it contain enough gold, so subdivided by the time it reaches the flotation-cell as to suffice for froth-making. The tailing from a vanner is not as suitable for the agitation-froth process as the pulp before it has undergone concentration on the vanner. Similarly, a gold-quartz ore containing 5% gold-bearing pyrite or other sulphides is better adapted to agitation-frothing than one containing 1% only. This applies to the mechanical stirrer; it does not apply to the pneumatic machine, in which air-bubbles, supplied lavishly, rise quietly through the pulp. In such a machine it is not necessary to have a large proportion of mineral for stabilizing the froth because the plentiful supply of bubbles obviates that requirement. As one bubble breaks, another is ready to take its place, so that the float, or concentrate, does not fall, but is lifted successively until it passes over the lip of the cell.

Another important phase of the subject is the recovery of the base metals associated with the precious metals. In mills using amalgamation and cyanidation, the presence of base-metal sulphides may be so detrimental that an ore containing any con-

siderable percentage of them is likely to be left in the mine. In some cases the presence of base-metal sulphides, insufficient to be a source of revenue, but sufficient to interfere with the milling, has rendered it unprofitable to treat an ore. For such mines the use of flotation comes as a real boon. In the San Juan region of Colorado at this time there is a pronounced growth of productive activity because flotation has facilitated the recovery of the base metals associated with the precious, and so long as the metal markets remain propitious, we may expect a further expansion in this direction. Flotation is superior to any of the older wet processes—amalgamation, chlorination, and cyanidation—in that it will enable the miner to recover not gold and silver only, but copper, lead, and zinc as well.

These general remarks will serve to introduce some analyses of specific conditions—a more satisfactory method of discussing a problem that is economic as well as scientific.

North Star.—Early in 1916 the management of the North Star Mines, at Grass Valley, undertook a critical analysis[4] of the milling methods then in use, with a view to consolidating the existing plants and obtaining greater economy of treatment. The ore was being reduced in two 40-stamp mills, each with a cyanide annex, situated at the two main openings of the mine. The combined capacity of the two plants was 110,000 tons per annum, development work during 1915 had been highly successful, and it was anticipated that by centralizing the entire plant at one shaft a considerable saving in operating expense might be made.

The ore was being crushed by 1050-lb. stamps to pass 20-mesh screens, the treatment involving amalgamation in the mortars and on plates, then table concentration, followed by classification into sand and slime for separate cyanidation. The concentrate was re-ground in tube-mills to pass 200-mesh and treated in the slime-plant. The total extraction averaged $10 in gold per ton of ore; of this, $5 was obtained in the stamp-mortars, $3 on the amalgamating plates, and $2 from the concentrate,

[4] For this information I am indebted to William Hague, managing director of the North Star Mines.

sand, and slime. The tailing averaged 25 to 35 cents per ton, so that the extraction averaged 97%. To treat 108,000 tons in 1915 the cost of milling was $51,000, for cyanidation $42,000, a total of $93,000, besides the tailing-loss of $30,000—a total deduction of $123,000.

Whatever process might be adopted, it was deemed advisable to retain amalgamation, since fully 50% of the gold extracted was caught in the mortars and 30% on the plates. It seemed wise to use amalgamation to catch as much of the free gold as possible early in the operations, as a sportsman tries to shoot his bird with the first barrel rather than the second.

The necessary experiments in flotation were made by the firm of Hamilton, Beauchamp & Woodworth, of San Francisco. Samples of plate-tailing were sent to them. The assay-value of these samples ranged from $2.50 to $2.90 in gold per ton. The first tests indicated that the material required re-grinding, to pass 80-mesh, in order to obtain a good recovery in the flotation-cell. When the heading assayed $2.50 the residue from these tests ranged between 10 cents per ton on pulp ground to 200-mesh, and 40 cents on pulp reduced to pass 65-mesh. When the plate-tailing was ground to pass 80-mesh the flotation residue averaged 25 to 30 cents per ton, like the residue after cyanidation.

The treatment of the flotation concentrate was the next step in the investigation. To ship the concentrate to a smelter—the Selby smelter, near San Francisco—would cost $17 per ton, for sacking, haulage, freight, treatment, and losses. This cost, on an ore containing $3\frac{1}{3}$% sulphides, would mean 50 cents per ton of ore. Smelting therefore was not to be recommended. There remained the possibility of cyaniding the concentrate. The ratio of concentration being 30 to 1, the flotation product was worth from $70 to $90 per ton. The residue from the working-tests, when cyaniding the flotation concentrate, averaged $6 per ton. The average consumption of cyanide was 6 lb. per ton. Experiments were made also to learn what effect the flotation-oil had on the precipitation of the gold or on the fouling of the cyanide solution. The results indicated that no difficulty was to be antici-

pated from the presence of small quantities of oil in the concentrate.

Given the results of these flotation experiments and comparing them with the results obtained in cyanide practice, it appeared that three methods were available for use in the consolidated plant which was to treat 110,000 tons per annum:

No. 1. To use 60 stamps of 1500 lb. each and crush to 0.04 inch diameter, employing amalgamation, classification, concentration of the sand, the classifier overflow and the concentrator tailing each going by separate conduits to the cyanide plant; the concentrate to be re-ground to 200-mesh and to undergo separate treatment in the cyanide annex, in order to ensure sufficient contact with the solution before being delivered to the slime-plant.

No. 2. To use 40 stamps of 1500 lb. each, crushing to 8-mesh, followed by amalgamation, classification, and re-grinding; to re-grind 70% of the stamp-product in tube or ball-mills to pass 80-mesh, this product to be treated by flotation, re-grinding the flotation concentrate to 200-mesh before cyaniding it.

No. 3. The same as No. 1 except that, instead of cyaniding the slime, to treat everything finer than 150-mesh by flotation and to leach the coarser material with cyanide solution; the flotation concentrate to be cyanided with the re-ground product of the water-concentrators.

Tests made in the mill showed that the 1500-lb. stamp falling 6 inches 105 times per minute would crush a little more than 5 tons per day to 0.04 inch, the screen having an open area of 36%; and also that this weight of stamp, crushing to 8-mesh, would have a duty of 7½ tons, yielding a product 70% of which would be coarser than 80-mesh.

The question of using ball-mills, both as primary and secondary crushers, had to be considered. The fact that 50% of the gold could be saved in the mortars was favorable to the retention of the stamps. Furthermore, in referring to descriptions of South African practice, it was noted that from 5 to 10% less gold was recovered by amalgamation after coarse crushing followed by tube-milling was introduced. If 5% more of the gold in the North Star ore, formerly saved by amalgamation, were thrown

into the cyanide annex, the extra loss in cyanidation would offset the saving of power and supplies to be anticipated from the substitution of ball-mills.

In estimating the operating cost of the 60-stamp mill and cyanide annex, the management was able to supplement its own experience with that of a neighboring plant having a capacity equal to that of the one being planned. In estimating the cost of flotation treatment, the North Star management was less confident, having to depend largely upon the advice of others; but by giving due weight to the evidence available it was possible to come to a fairly trustworthy conclusion, namely:

No. 1 method applied to 110,000 tons in one year, involved a working cost of $75,000, plus a tailing-loss of $33,000, making a total deduction of $108,000.

No. 2 would require a working cost of $69,000 on the same tonnage and in the same time, plus a tailing-loss of $27,000, plus a loss of $20,000 more (3300 tons of flotation concentrate per annum in which $6 per ton would be left after cyanidation) in the residue of flotation concentrate after cyanidation. The total deduction would be $116,000.

No. 3 required an operating cost of $75,000, plus a total tailing and residue loss of $39,000, making $114,000. In this estimate, as in No. 2, royalty has not been included in the operating cost.

The capital cost to be incurred was estimated at $52,000 for No. 1, $42,000 for No. 2, and $50,000 for No. 3 method.

It was decided that the saving of $15,000 per annum to be made by consolidating the plant, under No. 1 method, was justified, this decision being strengthened by the disadvantage, occurring under No. 2 and 3 methods, of having " to choose between paying a royalty or fighting a patent suit."

A Mexican Mill.—Next I shall quote figures relating to a silver mine in Mexico. The question had arisen of substituting flotation for cyanidation. Experiments, made by the same firm as had tested the North Star ore, indicated that this Mexican ore was amenable to flotation. The silver sulphides floated readily; the recovery ranged from 70 to 83% of the combined silver and

gold, varying according to the proportion of oxidized minerals in the ore—oxidation being a deterrent to flotation, of course. This compares with an extraction of 91% by the existing method, which gives 77% of the metallic content as bullion and 14% as concentrate. But a closer analysis of more detailed data is required to make a trustworthy comparison. The present method of treatment includes crushing in cyanide solution followed by concentration of the sand on Wilfley tables and of the slime on Deister tables, re-grinding the sand and cyaniding an all-slime product. The capacity of the plant is 150,000 tons per annum and the ore assays $10.50 per ton when silver is worth 65 cents per ounce. The ratio of gold to silver in the ore is 10 oz. silver to 0.07 oz. gold. The tailing is worth $1 per ton. The total cost of milling is $1.55 per ton, to which must be added 10 cents per ounce of fine metal for marketing the bullion, this charge including export-tax, expressage, and refining, and 15 cents per ounce of metal for marketing the concentrate, this expense including taxes, freight, smelting, and sacking. The present output yields a bullion 700 fine and approximately 50 tons of $350 concentrate per month.

On the other hand, the flotation plant would cost $50,000 and would produce 100 to 150 tons of $500 to $800 concentrate, to be marketed at a cost of 15c. per fine ounce and leaving a tailing assaying $2.10 per ton. The Mexican export-tax on concentrate is 2% (of gross value) more than on bullion, thus:

	Bullion, %	Ore, %
Federal	5	7
State	2½	2½
Total	7½	9½

The final comparisons are as follows:

1. Between table-concentration followed by cyaniding and straight flotation, the saving in cost of treatment by flotation is about equal to the extra recovery by tabling and cyaniding, but the increased expense for marketing the large tonnage of lower-

grade concentrate plus lower smelter-returns on concentrate than on bullion represents a loss of 90 cents per ton of ore by straight flotation.

2. Between table-concentration and cyanidation, as against flotation and cyanidation of flotation tailing, the extra recovery is 33 cents (extraction 94%) and the saving in cost is 57 cents per ton, while the additional expense of marketing the concentrate plus lower smelter-returns on concentrate than on bullion is 90 cents, so that the difference is extinguished.

Cyanide is taken at 30 cents per pound, 1.8 to 2 lb. being consumed per ton of ore. Lately the precarious character of the cyanide supply has furnished an argument in favor of flotation. Packing the concentrate on mule-back or freighting it by train, with the uncertainty of getting cars for shipment to a smelter, possibly outside Mexico, are points requiring careful consideration. The smelter deductions are important; usually payment is made on 95% of the silver and $19 (or 91.92%) is paid per ounce of gold in the form of concentrate against 100% of these metals in the form of bullion. This represents a net loss of 6 to 8% on this class of ore. At present therefore it is inadvisable to spend $50,000 in erecting a flotation plant to obtain a result no better than that given by the existing system of treatment, but it may prove advantageous in the future to adopt flotation followed by cyanidation when the flotation product itself can be treated safely and profitably on the spot, yielding bullion. This example will serve at least to emphasize the fact that such problems cannot be settled in the laboratory, and to show that the object of metallurgy is to give the greatest net returns rather than the highest percentage of extraction.

The Melones Mill.—Another interesting comparison between cyanidation and flotation is afforded by an investigation made by the Melones Mining Company, which treats a low-grade gold ore typical of this part of the Mother Lode region. The existing plant consists[5] of 100 stamps weighing 1000 lb. each, and dropping 6 inches at the rate of 107 drops per minute. The stamp-duty,

[5] For most of the information in these paragraphs I am indebted to W. G. Devereux, manager for the Melones Mining Company.

when discharging through a 20-mesh screen. is 5.3 tons. No plate-amalgamation is attempted inside the mortar, but mercury is fed into the battery, and the pulp when discharged passes over the usual amalgamating-tables. The ore, a gold-bearing quartz containing pyrite, averages $3.65, from which $1.83, or 50%, is extracted by amalgamation and cyanidation, leaving a 51-cent tailing and 3.4% of concentrate assaying $36 per ton. The further extraction of the gold in the concentrate may be disregarded for the moment. Of the total extraction 43% is obtained as amalgam, 17% as bullion in the cyanide annex, and 40% in concentrate, which also is treated by cyanidation. The pulp from 60 stamps passes from the amalgamating-tables to Wilfley concentrators, while that from the new mill of 40 stamps undergoes classification in spitzkasten before being concentrated. It has been observed in the Mother Lode region that the pulp from the stamp-battery does not concentrate so well after hydraulic classification as without such preliminary treatment. Sizing seems to be preferable. On the Wilfley tables the gold-bearing pyrite is recovered as a concentrate; at the same time, by the addition of extra water in the feed-box of the Wilfleys, the sand and slime are separated without the intervention of the usual desliming classifiers. The sand, assaying $1.15, goes to the leaching-vats of the cyanide annex; the slime, assaying $1, passes through cone-classifiers, the underflow from which joins the sand in the leaching-vats, while the overflow runs to the slime-plant. This includes Dorr de-waterers and Devereux agitators,[6] followed by Dorr thickeners and an Oliver filter. A middling, assaying $8 per ton, is made on the Wilfleys; this, after classification, goes to six " finishing " Wilfley tables, the tailing from which is passed to the sand-plant.

The following facts are pertinent to our inquiry. The Wilfley tables recover 95% of the gold that is so intimately associated with the pyrite as to have escaped amalgamation; such gold-bearing pyrite as escapes into the cyanide annex is either in the form of slime or it is material that has been insufficiently pulverized. The pulp after concentration on the Wilfleys assays $1.12,

[6] For a description of these machines see *M. & S. P.*, March 3, 1917.

whereas the mill-tailing, discharged from the cyanide annex, assays 51c. per ton. That represents the residual loss, to which must be added the loss in the treatment of the concentrate. The "sand" and "slime" are nearly equal in weight. The extraction of gold from the "sand" and "slime" together is about 55%, that is, 55% of the 31% of gold remaining after amalgamation and concentration. A solution containing ½ lb. KCN per ton of ore is used in cyaniding the slime, and a 4-lb. solution on the sand. The total cost of milling (excluding concentration) is 50 cents per ton of ore.

What can flotation do on this ore? Samples were sent to the Minerals Separation people in San Francisco and they reported thus:

	Weight, %	Gold, oz.	Recovery, %
Heading	100.0	0.06	100.0
Concentrate	1.4	1.83	42.7
Middling	6.2	0.20	20.7
Tailing	92.4	0.02	30.8

This showed a recovery of 63.4%, including the middling, which, in mill-practice, would be re-treated continuously. However, account is rendered for only 94.2% of the total gold in the heading. The material tested was slime from the Wilfley tables, the screen-analysis showing 98% through 200-mesh. In a later test, made at the same laboratory, a sample of the pulp as it came from the amalgamating-tables was subjected to flotation, the result being a failure owing to the coarseness of a large part of the product. After the sample had been re-ground, until only 4% remained on a 200-mesh screen, the flotation machine did as follows:

	Weight, %	Gold, oz.	Recovery, %
Heading	100.0	0.085	100.0
Concentrate	1.7	4.400	88.4
Tailing	98.3	0.010	11.6

The chief engineer (E. H. Nutter) for Minerals Separation reported that this test "indicates very definitely that the ore as submitted can be given flotation treatment usefully," but it must be noted that the sample "as submitted" was much too coarse to undergo successful flotation. The extra cost of re-grinding to 200-mesh is a vital factor in the problem. What would be the cost of re-grinding? At a neighboring mine, producing a similar ore, the cost of re-grinding is 25c. per ton. But all the pulp would not have to be re-ground; only the sand, say, 275 tons in all, out of the daily output of 530 tons. At 25c. per ton on 275 tons, the cost per original mill-feed would be 12c. per ton for re-grinding.

A flotation plant to treat 530 tons of such ore would cost $6000 f.o.b. San Francisco, or $10,000 erected; but the necessary re-grinding plant would cost $20,000 more. The items of operating cost are estimated, by Mr. Nutter, as follows, per ton of dry ore:

	Cents
Reagents	6
Labor	5
Power (35 hp. per 200-ton unit)	2
Royalty at 25c. per oz. gold	2
	15

To this must be added the present cost of crushing and amalgamation, which is 20c.; so that the total cost of combined treatment, to the point of making a concentrate, would be

	Cents
Crushing	20
Re-grinding	12
Flotation	15
	47

This compares with the present cost of 50c. Allowing a 90% recovery by flotation, as against the present 86%, on a $3.65 ore, the additional winning would be 14.6c. per ton.

The Melones concentrate, representing 3.4% of the weight of ore, is re-ground, at a cost of 50c. per ton, to pass 200-mesh and

is then cyanided, without roasting. The cost of treatment is $5.50 and the extraction is 92%. The cost is 19c. per ton of crude ore and the tailing retains 9½c. in gold.

In making this comparison the treatment of the concentrate is assumed to be the same, whether it be the product from the Wilfley tables or from the flotation-cells. No doubt exists as to the successful treatment of the flotation concentrate, which would not require re-grinding, so that the present cost of re-grinding the concentrate, which is 50c. per ton of concentrate, or 1.5c. per ton of mill-feed, would be saved. Moreover, the concentration would be higher, if one may judge from the results of the test made on the re-ground pulp. In that experiment the concentrate was only 1.7%, but it assayed $88, that is, it was half in quantity and double in richness as compared with the Wilfley product. Apparently the re-grinding had liberated some gold, which had become included in the concentrate; on the other hand, some of the quartz attached to pyrite had been loosened so as to join the rest of the gangue in the tailing. The reduction in the weight of concentrate would decrease the cost of treating concentrate from 19c. per ton to, say, 15c. The higher-grade concentrate would require more careful handling, and the extraction, at the same ratio of 92%, would leave a higher residue, namely 8% of $88, or $7.04, as compared with 8% of $36, or $2.88, making a difference, however, of only 2c. per ton of original ore, owing to the higher rate of concentration by flotation. In the event of adapting flotation to a stamp-mill, such as that of the Melones, it would be advisable to take the pulp from the amalgamating-tables to the re-grinding machinery, in preparation for flotation, and not to attempt any table concentration, because flotation would be better when leaving the pyrite in the pulp than when treating pulp after concentration. It only remains to remark that the Melones treatment might be changed to all-sliming and cyanidation, discarding concentration and separate treatment of the concentrate.[7]

The cost might be reduced 3c. per ton, but it must be re-

[7] Compare this with the Nickel Plate experience. "The Nickel Plate Mine and Mill." By T. A. Rickard. *M. & S. P.*, January 20, 1917.

membered that the flotation figure is only an estimate as against the actual cost by the existing method. The increased extraction might be 15c. per ton. The total gain, of 18c. per ton, would be attractive if confirmed by further experiment, and if the use of flotation did not involve inquisition by, and subservience to, a patent-exploiting company. That undoubtedly, in my opinion, is a deterrent now. If it were a question of erecting a mill on a mine that had no reduction plant, and that produced ore of the kind we have been discussing, it would be rational to adopt flotation, not only for the sake of the small extra extraction but on account of the first cost of plant. The Melones cyanide plant cost $50,000.

The Dutch-App Mill.—At the Dutch and App, a neighboring group of mines, in Tuolumne county, a conventional Californian mill of 40 stamps of 1050 lb. each, followed by amalgamation and concentration, has been changed from concentration by Wilfley tables and Frue vanners to flotation, so that a closer comparison is possible. I am informed [8] that the cost in the old mill was 74 cents, of which 38c. was for stamping, amalgamation, and concentration, and 36c. was for the transport and treatment of the concentrate. The Californian custom of reporting the cost of milling without including the expense of realizing upon the concentrate is misleading; so also is the practice of ignoring the loss or smelter-deduction from the assay-value of the concentrate. This item should be added to the assay of the mill-tailing in order to ascertain the total loss, and therefrom the total extraction of valuable metal. Thus the total cost in the old mill was 74c.; in the modified mill it was found to range between 88c. and $1 per ton. The modified plant, however, is at best a mill patched up for the purpose of testing the ore by flotation; therefore, the cost should be much reduced. The tonnage treated was at the rate of 200 tons daily, whereas the proposed new mill will treat 600 tons daily.

The tailing in the old mill, treating daily 200 tons of $3.75 ore, assayed 90 cents (excluding the loss in concentrate-treat-

[8] By W. J. Loring, who, I hope, at a later date, will contribute his own testimony on the subject.

ment), but when flotation replaced concentration by Wilfley tables and Frue vanners on the same grade of ore, the tailing was reduced to 35c. during the first month of operation, showing a saving of 55c. per ton. The comparative cost of a plant to treat daily 200 tons of ore carrying 5% of concentratable pyrite is estimated under normal conditions as follows:

(1) Twenty stamps of 1250 lb. each, with two re-grinding tube-mills, plates, and vanners—including rock-breaker, $48,000.

(2) Same mill, using flotation in place of vanners, $55,000.

(3) Same mill, concentrating on tables, the sand and slime treated by cyanide, $65,000.

No. 3 does not include the treatment of concentrate, because it is the usual custom to send it to the smelter at Selby. It will be noted that, for a comparison of plant-cost, No. 3 must be compared with No. 2. Flotation has given a slightly higher concentration of the gold-bearing pyrite in the Dutch-App ore; thus:

Old mill, 4½% of $35 to $40 concentrate.

Flotation, 5% of $50 to $65 concentrate.

The cost of transport and treatment is 38c. per ton of ore. The cost of haulage, freight, and smelter deductions is $9.50 per ton of concentrate. The cost of stamp-crushing and ball-mill re-grinding together is 35c. per ton. The cost of flotation by itself is 15c., making 88c. per ton in all for the extraction of the gold.

When the new mill is treating 500 to 600 tons daily, it is expected to reduce the cost to 68c. and the tailing-loss to 20c. per ton.

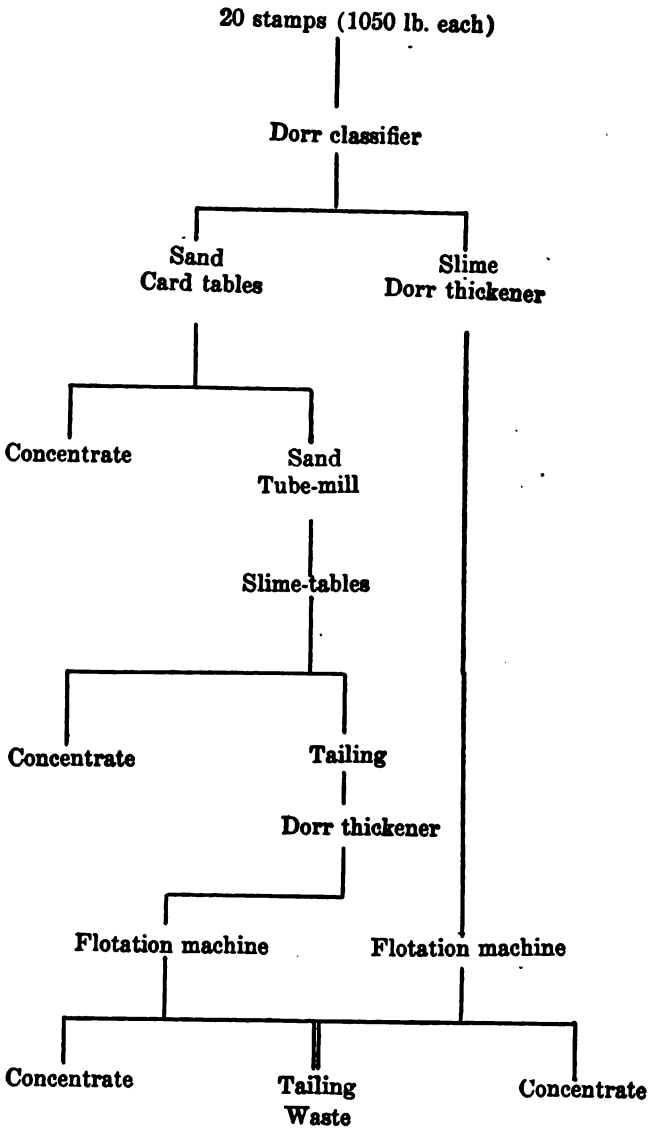
By way of further comparison I may quote the cost of milling at an up-to-date plant, using stamps, amalgamation, and table-concentration, namely, at the Plymouth Consolidated in Amador county, also on the Mother Lode. There the cost of milling is 36c. and the concentrate realization 24c. more, making 60c. per ton. The treatment is most satisfactory because, among other reasons, the yield of concentrate is only 1½%. On such an ore flotation would not be as beneficial as on the Dutch-App ore, which contains 5% concentratable gold-bearing pyrite.

The Argo Mill.—A tribute to the elasticity of the flotation process is furnished by the use of it in a plant treating custom ores. In the Argo mill, at Idaho Springs, Colorado, it has been found highly advantageous to substitute flotation for cyanidation, after stamp-milling and classification, as shown on the accompanying flow-sheet.[9] Most of the ore comes through the Argo (formerly Newhouse) adit, which taps the veins of Clear Creek and Gilpin counties. These contain gold and silver associated with pyrite, chalcopyrite, and tetrahedrite, so that it is a question of concentrating the sulphides encasing the precious metals. Much of the ore is of the so-called "free-milling" kind, that is, it is amenable to stamp-mill amalgamation. The coarse gold is caught on the tables before flotation; the fine gold is caught in the flotation concentrate. Good results are obtained by classifying before flotation, particularly on oxidized ore. A trial on an oxidized gold ore from the Paris mine yielded 86% by flotation and 98% by cyanidation. The mill levies the same charges for treatment as the smelter at Denver and has helped, by its competition, to lower the smelter-rates. Its own concentrate is sold to the smelter. Rens E. Schirmer, the manager, and Jackson Pearce, the metallurgist, informed me that they are able to treat ore assaying $40 to $80 per ton. They quote $10.50 for treatment on a $50, and over, ore, but the bulk of the custom ores that come to this mill range between $9 and $20 gross value, and on such material the milling-charge ranges from $4.75 to $5.50 per ton.

For zinc there is no pay and also no penalty.

For lead they pay the regular smelter rate, namely: "Deduct 1.5% from wet assay. The prices paid per unit for lead ore are based upon a quotation of $4 per hundred pounds, 1c. up or down for each change of 5c. in this quotation, which shall be 90% of the sales prices in New York of the A. S. & R. Co. for common desilverized lead, provided said price does not exceed $4 per hundred pounds. When price does exceed $4 per hundred pounds, the quotation used as a basis of settlement shall be $3.60

[9] See also an excellent article by Jackson A. Pearce. "Flotation Tribulations." *M. & S. P.*, Sept. 16, 1916.



Flow-Sheet of Argo Mill.

per hundred pounds, plus three-fourths the excess of said sales price above $4 per hundred pounds." [10]

For copper they pay on the dry assay, that is, 1% deduction from the wet assay, and the Western Union quotation for casting copper, less 6c. per pound.

For silver, they deduct ½ oz. from assays up to 10 oz. per ton, and pay for the remainder at 95% of New York quotation on date of assay. For ore over 10 oz. per ton, they pay 95% of the quotation, without further deduction.

For gold they pay $19 per oz. between 0.05 and 1.5 oz. per ton; on richer ore they pay $19.50 per ounce.

The Argo mill, with its flotation annex, has treated 4 oz. gold ore, 100 oz. silver ore, 40% lead ore, and 5% copper ore at different times. Such high-grade ore is mixed with the lower-grade before being milled. Money has been made even on a $1.25 ore.

It was found that the recovery by flotation was slightly better than by cyanidation; moreover, the cost was lower, owing to the less expense in chemicals. A much simpler flow-sheet became practicable; there is less pumping, less power, and less labor. Hence the adoption of flotation. A further and decisive advantage is the ability to beneficiate the base metals, notably copper, which was a cyanicide. Since flotation was introduced the mill finds a wider scope and is able to command a larger custom. The flotation machine in use is one devised and patented by Mr. Pearce. It is of the mechanical-agitation type, but it consumes less than one-third of the power required by the Minerals Separation machine previously used in this mill. A 6-cell Pearce machine requires only 5.3 horse-power. Two such 6-cell machines are employed, one to treat sand (80% + 200-mesh) and the other to treat slime. The former gives the higher recovery. I watched them at work and can testify that they produced a uniformly good froth and appeared to be operating admirably. Two pounds of an oil-mixture, consisting of two parts of gas-oil to one part of pine-oil (Pensacola Tar & Turp. Co.'s No. 400), is

[10] I quote the exact words in order that the reader may appreciate the hocus-pocus of this smelter method of fixing the price of lead. It is to laugh!

used per ton of ore. The gas-oil comes from Wyoming; it is one from which the lighter gasoline has been removed. The more sulphidic an ore the larger the proportion of oil required. As soon as sulphide particles appear in the tailing, more oil is added. Gas-oil costs 6c. per gal. and pine-oil 32c. laid down. The water is neither acid nor alkaline. Neither acid nor alkali is added. Fresh water is used, there being no return of water from the tailing. By using fresh water the millman avoids fouling of the liquid by an accumulation of colloids. Formerly the overflow from the concentrate-thickener was run back to the flotation-cell but it was found that this closed circuit tended to collect colloids detrimental to a high recovery by flotation.

Experiments have been made with as much as 40 lb. oil per ton of ore; the recovery was slightly higher than when using 2 lb. per ton. What a commentary on the "critical" point! When using 40 lb. of oil the bubbles are smaller owing to the larger proportion of gas-oil, which was increased to 85% of the oil-mixture. When using 5 to 6 lb. oil and storing the concentrate in a wooden bin, Mr. Pearce noticed that the oil seeped visibly.

Ordinary variations of temperature appear to have no effect. In winter the froth freezes occasionally, so that it sinks, but so long as the temperature is just short of freezing the operation is not affected. In summer the recovery is no higher than in winter. The mill recovers 92% of the gross market-value of the various ores and treats 100 tons daily.

The Portland Mill.—As yet scarcely anybody that has tried flotation has discarded it after trial. One example of such a reversal is furnished by the Portland Gold Mining Co. of Cripple Creek, and the reasons for it are interesting.

The ore was dump material assaying $2.25 per ton, carrying half an ounce of silver for every ounce of gold, both minerals being present as tellurides, chiefly calaverite. After treating over 100,000 tons the management decided that flotation was not superior to their older method of treatment by table-concentration and cyanidation, for the following reasons:

(1) Good extractions are obtained by cyanidation when grinding to 20-mesh, whereas flotation calls for grinding to 48-mesh.

This extra work costs 10c. per ton, which is a serious item on $2.25 ore.

(2) Cyanide bullion is sold to the Mint, and the small amount of concentrate that is made is so low in silica and so high in iron that it can be marketed at the smelter on easy terms, whereas flotation yields a large amount of silicious concentrate on which the cost of freight and treatment is three times that of marketing the by-product of a cyanidation mill. On this ore the recovery by flotation was found to be inversely proportional to the grade of the concentrate; a high recovery made a large amount of low-grade concentrate; a small amount of high-grade concentrate entailed a poor recovery.

(3) Only $20 per ounce was paid for gold in the flotation concentrate, and nothing for the silver. Cyanide bullion is sold to the Mint at $20.67 per ounce for gold and 95% of New York quotation for silver. Thus 4% more is received for the product from the table-concentrate than for the flotation product. On account of the highly silicious character of the latter it was found that the cost of marketing at the smelter was out of all reason, whereupon it was sent to the custom roasting-cyanide mills at Colorado Springs. This flotation concentrate proved ideal stuff to treat after roasting, but as the silver is not recoverable after the ore has been roasted, the mill could not pay for it.

(4) The royalty payable to the Minerals Separation company.

The principal difficulty was to make a high-grade concentrate and a low-tailing concurrently. Amorphous slime rises with the froth, and any effort to prevent it involves a loss of the sulpho-telluride mineral; in short, it is difficult to separate the gangue-slime from the mineral in this particular ore. Any free gold in the ore floats with the telluride and sulphide minerals. Incidentally, it is worthy of note that flotation in cyanide solution was accomplished successfully at the Portland by J. M. Tippett. He had to use caustic soda, in preference to lime, in order to ensure sufficient alkalinity. The ore was ground in the presence of caustic soda and cyanide. Mr. Tippett avoided de-watering, and the consequent loss of cyanide, by establishing a closed circuit. The pulp flowed from the flotation-cells to thickeners and

Pachucas, and thence to filters. By this method of treatment he was able to obtain a 4oc. tailing on a $20 ore. From $17 to $18 was taken off in the form of a 12-ounce flotation concentrate, the tailing from which assayed $2 or $3 per ton and was reduced to 4oc. by treatment in a Pachuca.

Summary.—In most cases the substitution of flotation means the making of a concentrate instead of bullion. The latter is ready for the market and easily handled or transported. The concentrate is bulky and if it has to be shipped elsewhere for treatment the handling of it entails loss, to which must be added freight and smelter deductions. However, these are troubles that can be obviated if the concentrate is treated at the mine. Some difficulty is said to have been caused by the oil retained by the concentrate; it may interfere with cyanidation, as Paul W. Avery testifies,[11] but we have the statement of E. M. Hamilton [12] that he has treated several samples of flotation concentrate with complete success. The experience at the Melones mine is to the point. Speaking generally, I infer that if an ore can be cyanided, then its concentrate, obtained by flotation, can also be cyanided successfully. In short, any gold and silver ore that can be amalgamated or cyanided is amenable to flotation, and the resulting concentrate is equally amenable to treatment by cyanidation. In some cases, as with Cripple Creek tellurides and the Cobalt silver minerals, it may be necessary to roast first, but the use of flotation on precious-metal ores need not involve dependence upon a smelter. That is important. On the concentrate made at Cobalt, for example, the total cost of marketing is $38 per ton. A chloridizing roast followed by leaching appears to be the only escape from this exaction. In California, the marketing of concentrate from a Mother Lode mine involves a cost, in freight, treatment, and other deductions at the smelter, of $9 to $15 per ton. This can be avoided, at many mines, by cyanidation on the spot without roasting, at a cost of about $5 per ton.

Thus we see that the substitution of flotation for the older processes of amalgamation and cyanidation is an economic rather

[11] "Cyanidation of Flotation Concentrate." *M. & S. P.*, May 16, 1916.
[12] *M. & S. P.*, March 11, 1916.

than a metallurgic problem. In most of the specific cases discussed in detail it is safe to assume that if the manager were starting today to equip his mine with a mill, he would select the flotation process rather than the older methods, or make flotation a part of his flow-sheet. The scrapping of an existing, and expensive, plant is quite another matter. Usually the simple flotation plant would cost half that of the more complicated cyanide annex. Yet, in conversation with various managers, I have ascertained that the control or assumed control of the basic flotation patents by the Minerals Separation people is a strong deterrent. Most of us do not like to be inquisitioned by the agents of a patent-exploiting company, nor do technical men care to be placed under pledges of professional secrecy to anybody. The royalty on gold is only 25 cents per ounce and on silver $2\frac{1}{2}\%$, so that the tax is not onerous, but a tax of any kind is an irritation to most men, particularly when the right of the tax-gatherer is still undecided by the courts of law. If and when this question of Minerals Separation's right to collect a royalty is decided satisfactorily we may expect a wide extension in the application of flotation to ores chiefly valuable for gold and silver.

FLOTATION LITIGATION. I[1]

By T. A. RICKARD

THE story of American litigation over the flotation patents is interesting and perplexing. The first contest over the validity of the Minerals Separation company's principal patent was caused by James M. Hyde, who in August, 1911, introduced the use of froth-flotation at the mill of the Butte & Superior Copper Company,[2] applying the process successfully to a zinc ore carrying a small amount of lead. On October 3, 1911, suit for infringement of patent 835,120 was brought by Minerals Separation against Mr. Hyde. The trial took place before the U. S. District Court at Butte and there, on July 28, 1913, Judge Bourquin decided that the patent was valid "in respect to all claims in issue."

It will be well to outline the nature of the patent in suit. The first claim says: "The herein-described process of concentrating ores which consists in mixing the powdered ore with water, adding a small proportion of any oily liquid having a preferential affinity for metalliferous matter (amounting to a fraction of one per cent on the ore), agitating the mixture until the oil-coated mineral matter forms into a froth, and separating the froth from the remainder by flotation."

Claim No. 12 states: "The process of concentrating powdered ore which consists in separating the minerals from gangue by coating the minerals with oil in water containing a fraction of one per cent of oil on the ore, agitating the mixture to cause the oil-coated mineral to form a froth, and separating the froth from the remainder of the mixture."

[1] From the *Mining and Scientific Press* of April 14, 1917.

[2] This company did not produce copper, but zinc, lead, and silver. In 1916 the name was changed to Butte & Superior Mining Company.

The patentees—H. L. Sulman, H. F. K. Picard, and John Ballot—refer in their specification to the Cattermole patent, No. 777,273, in which mention is made of using "an amount of oil varying from four per cent to six per cent of the weight of metalliferous matter present," and they then proceed to explain:

"We have found that if the proportion of oily substance be considerably reduced—say, to a fraction of one per cent on the ore—granulation ceases to take place, and after vigorous agitation there is a tendency for a part of the oil-coated metalliferous matter to rise to the surface of the pulp in the form of a froth or scum. This tendency is dependent on a number of factors. Thus the water in which the oiling is effected is preferably slightly acidified by adding, say, a fraction of one per cent up to one per cent of sulphuric acid or other mineral acid or acid salt; the effect of this acidity being to prevent gangue from being coated with oily substance, or, in other words, to render the selective action of the oil more marked; but it is to be understood that the object of using acid in the pulp according to this invention is not to bring about the generation of gas for the purpose of flotation thereby, and the proportion of acid is insufficient to cause chemical action on the metalliferous minerals present. Again, we have discovered that the tendency for the oily substance to disseminate through the pulp and the rapidity with which the metalliferous matter becomes coated is increased if the pulp is warmed. The formation of froth is assisted by the fine pulverization of the ore, and we find that slime mineral most readily generates scum and rises to the surface, while larger particles have less tendency to be included in the froth."

Application for this patent was filed on May 29, 1905, and the rights accruing under the patent start from this date. The patent was granted on November 6, 1906, and the life of the patent, 17 years, is measured from this later date.

Judge Bourquin's decision was sweeping.[3] It rested largely on a reply to the question whether Froment's British patent No. 12,778, of June 4, 1902, anticipated the patent in suit. On this point the Court expressed itself as follows:

[3] For full text of this decision see *M. & S. P.*, August 16, 1913.

"Froment's [patent] requires several times the quantity of oil that does this in suit, both by examination of the patents and working description and by tests in evidence. Froment crushes the ore in two operations, and de-slimes it before treatment, because the slime is too fine to be treated by his process, while the process in suit needs but one crushing operation, and finds slime advantageous and most easily recovered. Froment employs carbonate of lime; the process in suit does not. Froment requires acid, and in greater quantity and for a different function than does the process in suit, which latter may or may not use acid. Both may use heat, and both require agitation—Froment's agitation only to disseminate the oil, the process in suit for that purpose and also to aerate. Froment's result is by flotation by gas generated *in situ;* this in suit is by flotation by air introduced by vigorous agitation. Froment's product is like unto a magma, a spongy, pasty mass of oil and metallic particles, and more or less gas-bubbles, while this in suit is a froth of oil and metallic particles and air-bubbles. Froment's requires oil in such quantity that he deems it worthy of recovery from the concentrate, so far as it can be; this in suit so little oil it disappears, is not sensible to sight or touch upon the concentrate but only to analysis. In Froment's it would seem that the metallic particles are floated like the basket of a balloon, while in this like the very envelope of a balloon. Froment's is costly, while this is cheap. And from the evidence it would seem that Froment's process would fail in practical operation, while this in suit has succeeded. In Froment's he oils the metallic particles by agitation; then, when the mixture is quiescent, generates gas therein by quick reaction, followed by immediate and direct rising of the gas-bubbles to the surface in which they may come into contact with but few metallic particles. In this in suit vigorous agitation of the mixture beats great and excess volumes of air therein, likely bringing the ultimate air-bubbles into repeated contact with many metallic particles. The action of the gas in Froment's is almost explosive in nature. He speaks of the proportion of carbonate of lime to be sought as, in his test-tube example, the reaction may be so sudden and violent as to project the metallic

particles out of the tube. Froment's gas-bubbles, quick formed and quick rising it may be, arrive at the surface with expansion still in progress. These or analogous reasons may account for Froment's magma breaking gas-bubbles and fragile evanescent froth in so far as his result is like unto froth, and also may account for the process in suit's strong and lasting froth."

On appeal to the Ninth Circuit in San Francisco the decision of the lower court was reversed, on May 4, 1914. The opinion of the Court of Appeals, pronounced by Judge Gilbert, stated that " the fact that the appellees use a smaller quantity of oil than was used in the prior art is not of itself, and is not claimed by them to be, sufficient to distinguish their process so as to render it patentable." This Court held that " the agitating of the mixture to cause the oily-coated mineral to form a froth " was " clearly anticipated by the prior art." It is noteworthy that the Examiner of Patents rejected claim No. 12 " in view of 763,260, Cattermole, June 21, 1904; or 793,808, Sulman et al. July 4, 1905, . . . as expressing merely a difference of degree thereover as to the proportion of oily matter employed." Thus the Examiner refused to allow patentability on the mere use of a small percentage of oil. The claim thus cancelled, not the No. 12 of the final patent, quoted above, was the only one that was based exclusively on the use of a fraction of 1% of oil, without reference to a particular kind of agitation or a particular kind of froth. The Appellate Court took cognizance of this interesting disclosure for Judge Gilbert said:[4]

" We hold that to sustain the appellees' patent would be to give to the owners thereof a monopoly of that which others had discovered. What they claim to be the new and useful feature of their invention, as stated by their counsel, is ' agitating the mixture to cause the oily-coated mineral to form a froth.' As we have seen, that feature was clearly anticipated by the prior art, and when the elements of the appellees' claims are read one by one it will be found that each step in their process is fully described in more than one of the patents of the prior art, with the single exception of the reduced quantity of oil which they use.

[4] For the full text of this decision see *M. & S. P.*, May 9, 1914.

The patentees of the appellees' patent made a valuable contribution to the art in discovering the smallest quantity of oil which would produce the desired result. In doing so they pursued the course which all skilful metallurgists would be expected to pursue. They made a series of experiments to determine how small a quantity of oil could be used successfully. They found, as all must find who apply the oil-flotation process, that certain oils are adapted to use with certain ores, and that a larger quantity of oil is necessary for one kind of ore than for another. The appellees admit that for some ores they use four times as much oil as for others. Their discovery that a small fraction of one per cent of oil is sufficient to produce flotation of the metalliferous matter cannot, as we have seen, be made by itself or in a combination the subject of a patent. The appellees cannot take from others the right to use oil economically. This was evidently the ruling of the Patent Office on their application for a patent. One of their claims in the original application was 'the process of concentrating powdered ore, which consists in separating minerals from gangue by coating the minerals with oil in water containing a fraction of one per cent of oil on the ore, and recovering the oil-coated minerals.' This was rejected in view of the Cattermole patent 'as expressing merely a difference of degree thereover as to the proportion of oily matter employed.' Counsel for appellees admit that the claim was properly rejected for the reason that it leaves out the agitation and froth, and say 'our invention is something else than the mere reduction of oil.' "

Thereupon Minerals Separation obtained a hearing before the Supreme Court of the United States on a writ of certiorari. The case was argued in October, 1916. The court expressed its opinion through Mr. Justice Clark on December 11, 1916. It was laid down that the patent was valid on three counts: (1) the use of a " critical " and minute proportion of oil, (2) the use of a particular kind of agitation, namely, " by beating air into the mass," and (3) the production of a " peculiarly coherent and persistent " kind of froth. The most important parts of the opinion are to be found in three paragraphs.[5] The first defines the patent:

[5] For full text see *M. & S. P.*, December 30, 1916.

court will be that the patent is valid as to claims No. 1, 2, 3, 5, 6, 7, and 12, and that the defendant infringed these claims, but that it is invalid as to claims 9, 10, and 11. Claims No. 4, 8, and 13 were not considered in the degree of the two lower courts and are not in issue in this proceeding."

Meanwhile a number of Western mining companies had begun to use flotation. One of them was the Miami Copper Company, in Arizona. On October 10, 1914, suit was brought by Minerals Separation for infringement of patent No. 835,120 and also of No. 962,678 and 1,099,699. The first trial took place in the District Court at Wilmington, Delaware, and the decision, by Judge Bradford, was pronounced on September 30, 1916.[6]

In this case the issue differed from that involved in the previous litigation. Hyde had denied, not infringement, but the validity of patent 835,120. The Miami company denied infringement, claiming that it was using a method similar to that described in a patent of earlier date, namely No. 793,808. Judge Bradford accepted this contention. He said:

"The evidence shows that the defendant in its concentration of ore in its pneumatic flotation plant employs the process of patent No. 793,808, of July 4, 1905, to Sulman & Picard, hereinbefore discussed, as modified by the use of certain apparatus, substantially the same as a portion of the apparatus, the operation of which is described in the above-mentioned Callow patent," namely, No. 1,104,755 of July 21, 1914, to John M. Callow.

He decided that the Froment patent was not an anticipation because "it does not appear that there was present in the Froment process the very minute quantity of oil of the first patent in suit."

The essential part of the Wilmington decision is that the diminution of oil to less than 1% of the weight of the ore is patentable. Judge Bradford said:

"On the whole I am satisfied that the first patent in suit must be sustained as to claims 1 and 12, but not as to claim 9. The two former are definite, specifying and limiting the amount of oil to be used; claim 1 mentioning 'a small proportion . . .

[6] For full text of this decision see *M. & S. P.*, October 14 and 21, 1916.

amounting to a fraction of one per cent on the ore,' and claim 12 'a fraction of one per cent of oil on the ore.' Claim 9 mentions 'a small quantity of oil.' This is so indefinite as to render the claim void, unless on consideration of the patent as a whole the claim can by construction be limited to the use of oil amounting to only a fraction of one per cent. The patentability of the process of the first patent in suit resides in the use of oil in the extremely minute proportion disclosed in the descriptive portion of the patent to effect separation of froth with its metallic particles from the remainder of the mixture by flotation. The amount there disclosed is not in excess of 'a fraction of one per cent on the ore' and may be only one-tenth of one per cent on the ore, or even less. If, then, by construction claim 9 should be so limited as to be restricted to the use of oil amounting to only a fraction of one per cent on the ore, that claim is in substance, though not in exact phraseology, the same as claim 1 for the reason that in any event from the nature of the invention it would be necessary to read 'by flotation' into claim 9, if in other respects valid. But a limitation by construction producing such a result is inadmissible. It is suggested by one of the plantiff's counsel in his consideration of claim 9, that one for the purpose of securing immunity from the consequences of infringement might use an oil useful in the process, and add to it an oil not useful as applied to his particular ore, and, on being sued for infringement contend, 'I am using 1.1% of oil. I do not infringe. I am using more than a fraction of 1% of oil.' But the existence of this possibility does not, I think, warrant such a construction of claim 9 as is urged; for the disclosure of the patent does not extend to the use of 1.1% of oil, but is limited to a fraction of 1%."

In regard to the second patent in suit, No. 962,678, of June 28, 1910, to Sulman, Greenway, and Higgins, the Court quotes part of the description in the patent:

"According to this invention the crushed ore is mixed with water containing in solution a small percentage of a mineral-frothing agent (that is of one or more organic substances which enable metallic sulphides to float under conditions hereinafter

Moreover, the Supreme Court differs with everyone that has passed on patent 835,120. It holds the Patent Office wrong for having granted indefinite claims, it holds the Butte court wrong in deciding that such indefinite claims were valid, it holds the San Francisco court wrong for invalidating the whole patent, by inference it holds the Wilmington court wrong for basing patentability on a small proportion of oil alone.

It is a curious fact that the practicability of producing an effective froth by means of more than 1% of oil was not tried on a working scale before these suits were started. Such experimental demonstrations as were made, out of court or before the judges, were apparently unconvincing, for the sufficient reason, I believe, that the minimum proportion was considered best even by the defendants, but as soon as the Supreme Court had given its opinion and placed so much emphasis on the " critical " proportion, the use of more than 1% of oil was applied successfully on a scale of over 1000 tons per day in the mills of the Utah Copper and Butte & Superior companies, in Utah and Montana, respectively. The " critical " point was proved fallacious early in 1917.

An appeal from the Wilmington decision was taken promptly by the Miami company to the Court of Appeals for the Third Circuit, at Philadelphia, where the case was heard in February, 1917. As was to have been anticipated, the appellees made the most of the Supreme Court's decision in the Hyde case, in so far as it defined and limited the scope of patent 835,120. Counsel argued that the Miami company had not infringed because its operations differed radically from those described in the Supreme Court's decision, both in the kind of aeration employed and in the character of the froth produced. Whereas Hyde, and Minerals Separation also, used mechanical means for causing violent agitation and for producing the " cauliflower " froth, as described by Mr. Ballot, the Miami company used a Callow cell, an inclined trough having a porous bottom through which compressed air at a low pressure was admitted, producing a froth without the aid of mechanical agitation, and the froth thus formed was described as thin, tender, and evanescent. This froth broke

composed of 'modified' air-bubbles, coherent and persistent enough to permit of recovery of the metal. That was the unique thing—the peculiarity adverted to by the Supreme Court. In defendant's practice the froth produced by it is similarly composed of 'modified' air-bubbles, and so is coherent and persistent enough to permit of recovery of the metal. There is no point and nothing of importance in the degree of coherency or persistency beyond and in excess of that required for the recovery of the valuable metal."

The decision of the Court of Appeals at Philadelphia is expected at any moment. Meanwhile it is to be noted that after Minerals Separation won the preliminary decision in the Hyde case at Butte they brought suit against the Butte & Superior company and moved for a preliminary injunction. This was in the autumn of 1913. The Butte & Superior case was brought before the same court as that in which the Hyde case was first tried, and this court, at Butte, ruled that no injunction would be issued if the Butte & Superior company would file a bond and also file monthly reports of its flotation operations with the Clerk of the Court. This condition was fulfilled. No injunction was issued and the case has rested in *statu quo* up to the present. The trial began on April 16, 1917. It proved most interesting because a number of new scientific witnesses were placed on the stand and in the course of their evidence they gave the results of recent research into the principles of flotation. In my article on this phase of the subject I have quoted from the testimony given by some of these gentlemen at Butte. As regards the legal argument, it is noteworthy that the "critical point" was demolished by the evidence of large-scale mill-operations in Arizona, Utah, and Montana, showing that the use of 20 to 22 pounds of oil, or over 1%, per ton of ore had given even a higher recovery than the 2 to 5 pounds heretofore customary in these mills.[7] The question was also raised, and answered, whether the excess of oil was inert. Minerals Separation shifted its ground so as to broaden its claims to cover all processes in which an air-froth is a factor, regardless of the amount of oil used.

[7] "Flotation—the Butte & Superior Case." *M. & S. P.*, July 28, 1917.

They repudiated the peculiar agitation, the extraordinary froth, and the critical proportion of oil on which they had obtained a favorable decision from the Supreme Court.

[Since the above was written the Court at Philadelphia has recorded its decision in the case of Minerals Separation *v.* Miami Copper Co. This decision, made known on May 24, 1917, was not unanimous, one judge (out of three) dissenting. The majority opinion upheld the validity of patent 835,120, but interpreted the Supreme Court's decision in the Hyde case as meaning that " invention resides not alone in the critical proportion of oil, but also in air and agitation." The Miami company was held to have infringed because it used agitation similar in " degree of intensity and time of duration " to that defined by the Supreme Court as characteristic of the patented process. Such infringement was due to the use of a centrifugal pump and a Pachuca tank before aerating the pulp in a Callow cell. Inferentially the opinion suggests that infringement would not have been found if the Callow cell had been used without the pump and the Pachuca, both of which were discarded by the Miami company before the trial began, but evidence to that effect was not in the record. Apparently the use of the pneumatic machine in flotation is validated. The Court says, concerning the Callow cell, "Aeration is direct and is not the result of or caused by agitation. On the contrary, agitation results from aeration, and such agitation, though present in some measure, is not even approximately of the violence and duration of the agitation of the patent." As it stands, the Philadelphia decision clears the ground in that it leaves free the use of the Callow cell, and other pneumatic machines of the same type, in conjunction with such agitation as was used in the prior art solely for the purpose of bringing the oil in contact with the mineral in the pulp; in other words, unless the use of flotation involves an agitation characterized by great intensity and long persistence it will not infringe patent 835,120. The minority opinion confirms this view, stating that " steps of the process ' agitating the mixture until the oil-coated mineral matter forms into a froth ' meant the novel *air-entraining* agitation which the patentees disclosed, and did not cover the

novel *air-releasing* agitation which the defendants disclosed." The majority opinion sustained the validity of patent 962,678 for a " soluble frothing agent," but tied it to a violent and persistent type of agitation. On the other hand, the exception made in favor of the Callow cell as not infringing 835,120, under given conditions, was not, apparently, made to apply to metallurgical operations under 962,678; so that the definition of what is a " soluble frothing agent " becomes crucial.]

Some reference to the previous litigation in England and Australia may be made, although it is now only of secondary importance. It is vital to the proper understanding of the patent litigation as a whole to recognize the fact that the decisions in the British and Australian cases did not establish the validity of the British equivalent of U. S. patent 835,120. That issue was not before those courts; indeed, the prior art, except as it had a bearing on the validity of the Elmore bulk-oil patents, was not under consideration. Moreover it was the Elmore bulk-oil patent of 1898 and not the vacuum-air patent of 1904 that was at stake. The question before the British and Australian courts was the validity of Frank Elmore's British patent No. 21,948 of 1898 and Stanley Elmore's British patent No. 6519 of 1901, the first the principal bulk-oil patent and the second a modification specifying the use of acid. No account was taken of the patents issued between the dates of these Elmore patents and the date of the Minerals Separation patent of 1905, nor was the question of how such intervening patents would affect the validity of 835,120 considered. To establish the fact that Elmore's bulk-oil patent is not valid or that the M. S. process is not the Elmore process does not prove anything with regard to the validity of the M. S. patent. That question was not before the British courts and it is remarkable therefore that these cases should have been cited at all in the American courts. The effect of the citation has been only confusing.

Most of the English suits were between Minerals Separation and the Elmores, or the company with which they were identified.

Personal quarrels and charges of bad faith were made in Sulman & Picard *v.* Wolf, in 1905, and in Ore Concentration Company [Elmores] *v.* Webster and others [the Minerals Separation group] in 1908, but the two cases involving basic patent-rights were both brought by the Elmores against Minerals Separation.

In the first case, ended in 1909, British Ore Concentration Syndicate, Ltd., and Alexander Stanley Elmore *v.* Minerals Separation, Ltd., the principal issue was the validity of the Elmore bulk-oil patents of 1898 and 1901 against the Minerals Separation process as described in British patent No. 7803, the equivalent of U. S. 835,120. The Court (Mr. Justice Neville) gave judgment against the Elmores and decided that:

(1) The selective action of oil for sulphides was known before Elmore obtained his patents, and was disclosed in prior expired patents.

(2) Elmore's patent was for a process wherein a large quantity of oil was used, sufficient to carry all the sulphides to the surface by the buoyancy of the oil.

(3) The Minerals Separation process used only an infinitesimal amount of oil for the purpose of attaching air-bubbles to the sulphides, causing them to float by the buoyancy of the air-bubbles, and did not infringe F. E. Elmore's patent.

(4) The use of acid in oil processes was known before A. S. Elmore obtained his patents and was disclosed in prior expired patents, therefore, Elmore's patent was not infringed by Minerals Separation.

The plaintiff appealed and the decision of the court was reversed, it being held that Minerals Separation was infringing the 1901 patent, involving the use of acid with oil. The Court of Appeals found that

(1) The first Elmore patent was not anticipated by previous expired patents [such as those of Robson and Everson].

(2) If Minerals Separation used a thin oil they would not infringe Elmore [who used a thick oil; so also Minerals Separation used a thicker oil (oleic acid) than is now customary in the United States].

(3) The second Elmore patent [that of A. S. Elmore of 1901] was not anticipated by previous expired patents [such as Everson's, in which acidulation is mentioned].

(4) Minerals Separation infringed the second patent by using acid.

An appeal was then taken to the House of Lords and on November 16, 1909, the judgment of the Court of Appeals was reversed, that of the trial court being upheld.

The Lord Chancellor (the Earl of Loreburn) said that the Frank Elmore patent of 1898 need not be discussed, because it had no place in the controversy, " into which it has nevertheless been introduced with no other result than to confuse the issue." He held that the Stanley Elmore patent of 1901 was " framed with great subtlety, being partly narrative, partly claim " and " designed in order that the claim might be expanded or contracted as occasion might require in the interest of the patentee; " that the only definite claim was for acidulation, and that this claim was anticipated by Everson; therefore the patent could not be sustained.

The Earl of Halsbury was of the opinion that the inventions of Elmore and Minerals Separation were " essentially different," the one being dependent on " the selective action of oil, the other upon surface tension "; that acidulation had been " invented and patented " before the date of Stanley Elmore's patent, and that this patent was so ambiguously stated that it should be held bad.

Lord Atkinson likewise described the specification of the patent as " framed, somewhat craftily, in terms of studied vagueness and ambiguity "; he held that it could not claim " the mere addition of acid in small quantities to a mixture of ore, water, and a relatively infinitesimal quantity of oil reduced to a ' freely flowing pulp.' " If the patent was for the addition of a small quantity of acid and a relatively large quantity of oil to a mixture of ore and water, where the oil, in accordance with some obscure law of affinity, seized upon the minute particles of ore in preference to the earthy particles, and, by the buoyancy of oil, floated them to the surface, then the Minerals Separation did not in-

the oil 'by its selective action coats or absorbs the metallic particles, sulphides, tellurides, and the like.' The whole mixture then flows over a weir and down an incline over a number of wave-like steps or baffles by which the stream of pulp and oil globules is thrown against an oiled apron continuously moving in the opposite direction. Separation is effected by the oiled surface of the apron taking up most of the oil globules and by also picking up from the pulp such particles of metallic substances as have escaped oil selection in the mixer. The patentee distinctly draws attention to the fact that separation in this apparatus does not depend upon the buoyancy of the oil, and that consequently tar, heavy residuum oils, and other like substances of a greater gravity than water may be employed as the selective agent. The question arises whether the selective action of the oil or tar when the separation is effected by the second apparatus differs from the selective action of oil when the separation is effected in the first apparatus. The answer is in the negative. The 'coating or absorbing' described in connection with the second apparatus is not different in character from the entrapping described in the first apparatus. The 'oil globules' hold and carry the metallic particles and are taken up by the oiled surface of the apron, which also picks up from the pulp such particles of metallic substances as have escaped selection by the oil in the mixer, that is to say, such particles as have not been coated and carried in the 'oil globules.'"

Throughout these British and Australian litigations the validity of the bulk-oil patents, of 1898 and 1901, and not of the vacuum patent, of 1904, was at stake. It is a curious fact that whereas the Elmore vacuum method depends upon surface-tension and the use of air quite as much as the Minerals Separation method, it was not cited in the litigation and it was ignored by the courts. It is also curious that during the six years of litigation in the United States the Elmore vacuum patent was not used to attack the validity of 835,120, although this patent of Minerals Separation was taken out in England on April 12, 1905, as compared with Elmore's vacuum patent of August 16, 1904. It may be asked, why did not the Miami company fall back on this de-

fence and use Elmore to fight the Minerals Separation? The answer is the fear to establish another patent monopoly, possibly no more pleasant than the one already on the ground. However, in May, 1915, after the Miami suit had been heard at Wilmington, the Elmore vacuum patents were purchased for $50,000 by a syndicate headed by Messrs. D. C. Jackling and J. Parke Channing, representing the Utah, Miami, and other important copper-mining companies in the United States. It is possible that the possession of these Elmore patents may prove an interesting factor in later litigation, but it is even more likely that the use of oil will be discarded before this litigation is ended.

FLOTATION LITIGATION. II*

By T. A. Rickard

Introduction.—In our issue of April 14, 1917, I told the story of the litigation arising in the Federal Courts out of disputes over the validity and scope of the patents owned by Minerals Separation, Ltd. At that time the Miami case had just been adjudicated by the Circuit Court of Appeals at Philadelphia, and the Supreme Court had disposed of the Hyde case. Since then the suit brought by Minerals Separation against the Butte & Superior Mining Co. has dragged its slow length through the three courts to final adjudication by the Supreme Court. This case may be regarded as a necessary sequel to the Hyde case. Meanwhile the Miami case has not yet gone to the Supreme Court; it is in the accounting stage, before a Master in Chancery, but it is expected that after the Master has reported finally, this case eventually will be submitted to the Supreme Court.

Two fresh suits have been started by Minerals Separation, namely, against the Nevada Consolidated Copper Company and the Magma Copper Company, the first operating at McGill, in Nevada, and the other at Superior, in Arizona.

Butte & Superior.—This case was tried first before Judge Bourquin in the District Court of Montana and a decision was given on August 25, 1917.[1] The trial lasted from April 18 to May 15. The Court upheld the validity of patent No. 835,120 and the Butte & Superior Mining Co. was declared to have infringed this patent. It was found that throughout the period of infringement the defendant's process always involved the use of "a

* From *Mining and Scientific Press* of January 22, 1921.

[1] The opinion was recorded in full in the *M. & S. P.* of September 29, 1917.

pyramid machine of seven cells in series, each cell containing a revolving perpendicular spindle and horizontal blades, and having two opposed spitzkasten." The result was violent agitation. At certain points in the flow-sheet there were, it is true, Callow or pneumatic cells, but at all times the pulp was first subjected to the rapid rotary agitation as described.

As to whether, after January 7, 1917, the addition of petroleum oil, to bring the total mixture to more than 1% of oil on the ore, took the defendant's operations outside the scope of the patent, the Court decided that the petroleum oil added in the mixture "if not inert is ineffective, wasted, and injurious to the process and results," and that the pine-oil, used in substantially the same proportion as during the admitted infringement before January 7, 1917, was performing the same function as before; therefore, the substance of the patent having been taken, the defendant could not escape the consequences of infringement.

An injunction and accounting were ordered by the decree of the District Court, but the injunction was stayed pending an appeal. This appeal was argued at San Francisco, before the Circuit Court of Appeals, on March 8, 1918,[2] and a decision was given on May 13, 1918.[3] The Court was not the same as that which had heard the Hyde case, for Judge Gilbert was absent, but Judge Ross, who wrote the opinion in the Butte & Superior case, was one of the three who had sat in the Hyde case. The chief question considered was the proportion of oil used in the process covered by the patent. The majority of the Court, Judges Ross and Hunt, appear to have been impressed by a colloquy[4] that took place between W. H. Kenyon, of counsel for Minerals Separation, and Justice McReynolds of the Supreme Court during the argument of the Hyde case. In consequence they held that the Supreme Court intended to limit the patent to five-tenths of 1% of oil on the ore, that

[2] A description of the proceedings appeared in the *M. & S. P.* of March 16, 1918.

[3] The full text of the decision will be found in the *M & S. P.* of May 25, 1918.

[4] See p. 379 of *M. & S. P.* of March 16, 1916.

being, in their opinion, the critical proportion that the Supreme Court had in mind when holding patentability to reside, among other things, in the use of a specific amount of oil "having a preferential affinity for metalliferous matter." Judge Morrow dissented, his opinion being that the patent was limited to 1% of any oil or oily liquid, and that the use of oil "in a quantity amounting to more than a fraction of 1%" was not an infringement upon the plaintiff's process.

This case was then taken, by writ of certiorari, to the Supreme Court, which gave its decision on June 2, 1919. The opinion [5] was written by Justice Clarke, as in the Hyde case. The Court held, against Judge Bourquin, of the Montana District Court, that "petroleum and petroleum products are oils useful in this process of the patent," and it agreed with the minority opinion of the Court of Appeals limiting the scope of the patent to 1% of oil. I quote the last paragraph of the Supreme Court's decision:

"It results that the decree of the Circuit Court of Appeals that the respondent infringed the patent only when using one-half of 1% or less of oil on the ore must be reversed, and that its implied holding that the use in excess of 1% on the ore did not constitute infringement must be sustained. The case is remanded to the District Court for further proceedings in conformity with this opinion."

It will be remembered that the Butte & Superior company increased its use of oil to more than 1% after January 7, 1917,[6]

[5] See *M. & S. P.* of June 21, 1919.

[6] In a statement dated November 22, 1919, and filed by the Butte & Superior company on the accounting, the varying portions of oil are given in detail. From September to December 1915, less than ½% was used; from January 7 to January 29 the percentage was well above 1%; from January 30 to February 9 it was less than 1% but more than ½%; from February 12 to March 31 it was again in excess of 1%, and so on. An interesting question arose, Minerals Separation insisting that the oil in the circulating load should not be included when determining the proportion of oil used vis-a-vis the patent. The oil in circulation, which is returned to the head of the mill, amounts to several pounds per ton on the ore. The Minerals Separation people contended that the Butte & Superior was in contempt of the injunction because it has added only 18 lb. of fresh oil during certain periods, and that the proper interpretation of the Supreme Court's decision required the addition of at least 20 lb. of fresh oil in the process in order to escape infringe-

that is, almost immediately after the Supreme Court's decision in the Hyde case. The same Court now held that the company, by which Mr. Hyde had been employed professionally, had infringed the patent only when it used oil in the proportion of less than 1%. In arriving at its decision, the Court made the following findings:

1. That the new evidence was too meagre in amount and too unsatisfactory to modify the Court's conclusion in the Hyde case on validity.

2. That except as to the proportion of oil, defendant's methods were substantially those of the patent in suit, that is, as defined in the Hyde case, the agitation of the pulp "by beating air into the mass" so as to form "a peculiarly coherent" froth.

3. That petroleum products are oils "efficient and useful in the process," but not "as highly efficient" as pine-oil or other oils that in the record are called "frothing oils."

4. That the froth derives its power of flotation mainly from the inclusion of air introduced into the mass by agitation.

5. That the patent disclosure to which Minerals Separation must be limited is when a fraction of 1% of oil is used "in the manner prescribed."

6. That the term "frothing oil" does not appear in the patent.

7. That "the patent is on the process, it is not and cannot be in the result," and the scope of the patentees' rights is limited "to the means they have devised and described as constituting the process."

These findings by the Supreme Court are important in their bearing upon further litigation. The idea of a frothing-oil [7] is rejected. So far as patent 835,120 is concerned, we have "oils, oily liquids, and oily substances having a preferential

ment. Judge Bourquin, of the Montana District Court, decided that there was no proper justification for the contention that the Supreme Court had so decided and advised Minerals Separation to appropriate subsequent procedure in the case with a view to having the question determined. The answer hinges upon effectiveness of the oil in circuit, and as to that there seems to be little doubt among those using the process.

[7] It is not an oil that froths; it is an oil for making froth.

affinity for metalliferous substances." In this (Butte & Superior) case the type of operation considered was that of the Janney machine, in which violent agitation is obtained of the type of the Gabbett mixer. Naturally it was inferred by those using machines of the pneumatic type, such as the Callow cell, that they could escape the charge of infringement, for did not the Supreme Court state the essence of the patent in the following definition: "We have found that if a proportion of oily substance be considerably reduced . . . granulation ceases to take place, and *after vigorous agitation* [italics mine], there is a tendency for . . . metalliferous matter to rise . . . in the form of a froth or scum." Again, the Court said: "The froth or scum derives its power of flotation mainly from the inclusion of air bubbles *introduced into the mass by agitation.*"

The Butte & Superior case was sent back to the District Court, in order that it might recast its decree in conformity with the decision of the Supreme Court. An accounting was ordered and an account was filed before Judge Bourquin by the defendant. Exceptions were taken thereto. At the same time Minerals Separation petitioned the District Court to adjudge Butte & Superior guilty of contempt for having violated the injunction issued by the Court, the contention being that Butte & Superior was *not* using more than 1% of oil mixture per ton, because a portion of the oil was returned with the middling to the head of the floation machine from the fourth to the seventh Janney cells. After a hearing (in February, 1920) Judge Bourquin dismissed the contempt petition, holding that this question had not been decided by the Supreme Court and that he therefore could not adjudge contempt upon a question that had only been half litigated by the plaintiff. Nevertheless, this is an important point, for, in most milling operations, a varying portion of the oil is re-used. The accounting in this case is still pending, no testimony having been taken as yet.

Miami Copper Company.—This case was decided in the Circuit Court of Appeals at Philadelphia on May 24, 1917. The majority opinion was that the three patents in the suit, No. 835,120, No. 962,678, and No. 1,099,699, were valid and

had been infringed.[8] The minority opinion held that the first patent had not been infringed by the defendants' operations except when using the so-called first method. This case is rendered interesting by the fact that the Miami company used four methods successively; in the first it used a standard Minerals Separation machine; in the second, a centrifugal pump, a break in the circuit, a Pachuca tank, and Callow cells; in the third a Pachuca tank and Callow cells; and in the fourth a bucket-elevator and Callow cells. The fourth did not appear in the record, the majority opinion concerning itself only with the three previous methods, all of which it adjudged to have infringed patent No. 835,120. The main question was whether the agitation in the Miami mill was of the violent and persistent kind covered by the patent, the Court deciding that the centrifugal pump and the Pachuca tank together produced that kind of agitation. The fourth method, from which these devices were omitted, was not discussed because the Court "cannot consider and adjudge with propriety or authority a process with respect to which the plaintiff has had no opportunity to produce testimony and which was not embraced in the decree [of the District Court] we are reviewing." This was unfortunate for the Miami company, which, since the case was first tried in the lower Court, has discarded the infringing devices. The company managed its case badly, for the real name of the Pachuca tank is the Brown agitator, and to contend that the passage of the pulp through a Pachuca did not "agitate" was unwise.

Since this case will be referred again to the Circuit Court of Appeals, and possibly to the Supreme Court, after the Master makes his report on the methods that have been used in the Miami mill since October 1, 1915 (the date at which the third method was discontinued), it is well to analyze the majority opinion, by Judge Woolley, because, obviously, it bears upon the highly important question whether aeration of the pulp through a porous medium, as in the Callow cell, constitutes infringement of No. 835,120.

It is to be noted, in the first place, that the Court of Appeals,

[8] See *M & S. P.* of June 16 and 23, 1917.

following the Supreme Court in the Hyde case, overruled the District Court when it said that the patentability of 835,120 resides in the mere diminution of oil. Judge Woolley interpreted the Supreme Court's decision as finding patentability in the co-action of a specific proportion of oil and a special kind of agitation, the air bubbles being introduced into the pulp "by an agitation greater than and different from that which had been resorted to before." The Miami company admitted the use of less than 1% of oil and that the lifting force in its three methods was air; the issue therefore was whether the agitation it produced was "greater than and different from" the prior art. It was admitted that a froth was formed, but it was denied that it was the same kind of froth as that of the patent or the product of the kind of agitation described in the patent.

Setting aside the first method employed at Miami as being obviously experimental, it will be noted that in considering the second method Judge Woolley decided that the centrifugal pump sucked air and that the blow of the pump-paddle produced the agitation of the patent as to violence if not duration. He found some aeration resulting from the splash of a break in the circuit; likewise he found agitation and aeration in the Pachuca tank. In normal operation of the second method the pulp did not come to rest in the Pachuca but was delivered by launders to Callow cells. The Court found that the entrance of air through the porous medium at the bottom of the Callow cell caused some measure of agitation but it was "not even approximately of the violence and duration of the agitation of the patent." The Court proceeded to say that the defendants had argued the case largely as though its process consisted solely in passing thoroughly mixed but quiescent pulp directly into Callow cells, where it received its first and last aeration without previous or present agitation, resulting in a metallurgical froth quite different from that of the patent. Judge Woolley could not find that the record justified this argument; he said:

"If the only agitation to which the pulp was subjected (after such agitation as in the prior art was necessary to mix

the oil and ore) was the agitation of the Callow cells, we would not say that that agitation amounted to or was the equivalent of the violent agitation of the patent disclosure and constituted infringement; . . . the Callow cells were not the whole process but were merely the last of four distinct parts of the process, the other three being the process of the patent or its fair equivalent. Having used the process of the patent in the first three steps [centrifugal pump, break in circuit, and Pachuca] in developing in the pulp the potentiality of the critical quantity of oil and air, and in bringing the pulp to the point where, if permitted, it would produce the result of the patent, we feel that the defendant cannot escape infringement by taking an additional step, even though that step if taken alone avoids the patent."

The foregoing quotation is the crux of the decision by the Court of Appeals in the Miami case; it shows what a blunder was made in adopting the unnecessary use of the machines that infringed the patent, for the Court, referring to the patentees, said that "agitation was the secret by which the principle of their discovery could be unlocked and used."

In the third method, the centrifugal pump and the break in the circuit were omitted, the Pachuca being preceded by a bucket-elevator, which performed the function of the centrifugal pump in raising the pulp. The oil, it is true, was added ahead of the elevator, but, without commenting upon the action of the elevator, the Court held that this method also involved an agitation similar to that of the patent and therefore constituted infringement.

The second and third methods were discontinued in September, 1915, four months after the submission of the case to the District Court, just one year before that Court handed down its opinion, and twenty months before the Court of Appeals pronounced its decision. For most of the time between October 1, 1915, and May 24, 1917 (the date on which the Court of Appeals issued its decision), the Miami company used the fourth method, consisting in the employment of the bucket-elevator, launders, and Callow cells, the mixture of oils being added at

the foot of the elevator. Although the flow-sheet of this practice was before the Court in the form of a blueprint and the questions involved in these operations were argued at length, the Court felt itself restricted by the record so that it could not "consider a process with respect to which the plaintiff had had no opportunity to produce testimony, and which was not embraced in the decree under review." Had the Court been of the opinion, as has been argued by Minerals Separation in later proceedings, that the second and third methods were of such scope as to include the Callow cell, there was enough in the record to warrant a consideration of this question. In discussing the third method, the Court reproduced in its opinion the blueprint mentioned above and described an experiment in which one part of the Miami mill was operated by the third method and another part by the fourth method. The Court said:

"In the experiment, one group was operated with the Pachuca tank as planned. In the other, the Pachuca tank was cut out and the pulp conveyed directly from the elevator to the cells. The result was no apparent difference in the action of the pulp and little difference in the assays of the metal recoveries, that difference, curiously enough, being in favor of the group in which the Pachuca tank was not used. The evidence of the fact and of the effect of this experiment was not contradicted, except, perhaps, by the defendant itself, by returning at once to its previous practice of using both Pachuca tanks, and in pursuing that practice to a time beyond the trial. This fact places the Third Process [9] in the position of the Second, where we have found that agitation and aeration of the Pachuca tank is the agitation of the patent, and amounts to infringement."

From the foregoing it is not quite clear whether the Court held that the method without the Pachuca avoided infringement, although the reference to the contradiction of the experiment by the return to the use of the Pachucas might warrant such an inference. In the direct testimony and cross-examination there was an account of the operation on a milling scale of the

[9] I have used "method" instead of "process," the former term suggesting more correctly a way of performing a process rather than a different process.

elevator and Callow cells, precisely as described under the so-called Fourth Process, and it is unfortunate therefore that the Court held itself unable to adjudge this point, so vital to the suit, and to the legal status of the Callow cell under the first patent No. 835,120. Moreover, the status of the Callow cell under the second (soluble frothing-agent, No. 962,678) patent was not discussed by either the District or the Appellate Court in the Miami case. This is a curious omission. The Court of Appeals had considered the use of the Callow cell in connection with the first patent, and found it not trespassing upon the agitation of that patent; if a different measure of agitation was intended to be ascribed to the second patent, and there was lack of proof of the agitating effect of the bucket-elevator under either of the patents, it was open to both Courts to apply the measure of agitation of the second patent to the Callow cell and thereby determine where it came within the scope of that patent. The question of the action of the Callow invention was known to the Court of Appeals to be *the* important issue involved in the lawsuit, and if there had been any intention of bringing the Callow cell within the scope of the second patent, it was to have been expected that the Court would so express itself, instead of leaving this vital question undetermined. In default of a clear pronouncement on this point, it may be assumed that the Court meant what it said when it found the difference between the first and second patents to be in the character of the frothing-agent used, and that in the second, as well as in the first, patent "the decision turns upon the kind and degree of agitation employed by the defendant." Since the third patent in suit is concededly an amendment of the second patent, it must be limited or fall with it.

After the decision of the Court of Appeals, in May, 1917, the Miami company was given time to decide whether it would present a petition to the Supreme Court for a writ of certiorari preliminary to a further review of the case by the court of last resort, and, after due consideration, the defendant company concluded to accept the decision of the Appellate Court as being substantially in its favor, any action in the

nature of an appeal therefrom having the appearance of an attack upon that favorable decision. Accordingly in August, 1917 the Miami company notified the Court of Appeals of its intention not to apply for a writ of certiorari, whereupon the mandate of that Court issued and the decree of the District Court was pronounced, together with an injunction restraining the Miami company from continuing the practices that infringed the patents in suit.

In accordance with the original order entered by Judge Bradford, of the District Court, the case was referred to William G. Mahaffy, as Master, to obtain an accounting of the profits derived by the Miami company in consequence of its infringing practices. Late in 1917 the Master ordered the Miami company to file its account, which was done in due course. Minerals Separation filed its exceptions to this account and thereby raised the question as to whether the milling practice subsequent to the first, second, and third methods, as considered by the Court of Appeals, was or was not a colorable departure from the declared infringements. In the support of its contention that the later practice was merely such a colorable departure, Minerals Separation called as its witness R. B. Yerxa, assistant mill-superintendent to the Miami company, and examined him for 30 days in connection with the introduction of 80 exhibits, representing every milling and experimental operation performed in the mill from September, 1915, to the date of the examination. Mr. Yerxa's testimony covers 625 pages. At the request of Minerals Separation, his testimony was interrupted in order to allow a visit of inspection to the Miami mill by the Master, with counsel and experts for Minerals Separation. This visit extended over four days.

On November 26, 1919, more than a year and a half after the taking of testimony had been begun before the Master, and after 2500 pages of testimony had been accumulated, Minerals Separation made a motion for leave to file a Supplemental Bill, the avowed purpose of which was to take from the Master the question whether the later operations of the Miami company were or were not infringing. Two months later, on

January 27, 1920, the Court denied this request, on account of certain defects in the proposed Supplemental Bill, and at the same time indicated its opinion that the investigation into the later milling operations came properly before the Master.

On May 4, 1920, Minerals Separation filed its petition in the District Court, praying that the Miami company be adjudged in contempt, as having violated the injunction of the Court, and that a further injunction be issued to restrain the company from the practice it had adopted after discontinuing the so-called Third Process. On May 24 the Miami company filed its answer denying that the said operations were infringing and asking that the petition be dismissed. This motion was argued before the Court on June 15, and on July 23 the Court dismissed the petition for contempt. Judge Morris, of the District Court, in his opinion, stated that "in view of the nature of the new processes used by the defendant as charged by the petition . . . the plaintiff must obtain the relief to which it is entitled, if any, touching the new processes, either through the proceedings now being had before the Master and the decree to be entered thereon, or by a new bill, and not otherwise." On the same day therefore Minerals Separation made a motion for leave to file a Supplemental Bill, praying that Minerals Separation North American Corporation be made a party to the cause, and, although objection was made to this, the Court decided to grant the request, "but without prejudice to the defendant to renew its objections, in a manner then suitable, to the bill when filed, if it be so advised." An order accordingly was made on July 22. Four days later Minerals Separation asked for leave to file a second Supplemental Bill, the purpose of which was the taking of the investigation of the Miami company's later practice from the Master, and the trial of the same before the District Court. This was denied, on August 11, 1920. Thereupon Minerals Separation took an appeal on the two orders (of July 23 and August 11) to the Court of Appeals, and the Miami company filed a motion to dismiss the appeal, and this matter was set for argument at Philadelphia on November 9. A month later, on December 9, Judge Woolley pronounced the

decision of the Court of Appeals, affirming the orders of the District Court and holding that the modifications or changes made by the defendant in its milling practice since September, 1915, were not plainly mere colorable equivalents of procedures that infringed. Judge Woolley held further that the practice of issuing supplementary injunctions is not to be adopted in the Third Circuit and that "the remedies against infringement after decree are those which now prevail, namely, damages and profits on accounting, attachment for contempt, and original bill; in the last the patentee's right to injunctive relief is fully preserved to him." The Court stated: "We have read and carefully studied the entire record . . . We shall not re-state the law of the case, but shall address ourselves solely to the new facts. These embody at least eleven new procedures or modifications of procedures charged to be infringements because equivalents of the infringements found by this Court in its decree. The processes decreed to be infringements were made up of several steps in which it was found, speaking most generally, that infringements were completed before the pulp had reached the Callow cells. In none of the eleven modified processes, again speaking generally, is there a centrifugal pump or a 'break in the circuit' or a Pachuca tank, means or steps held potential in the infringements found. In the later modified procedures, Callow cells are employed exclusive of and inclusive with other means, in some instances with no prior agitation, in other instances with prior agitation without aeration, in still other instances with prior agitation and aeration, indicating agitation in degrees varying as greatly as the adjectives used in describing it; but whether in any of them there is agitation of the kind, in the degree, and for the duration contemplated by the patent is not so clear and unclouded as to make the newly alleged infringing procedures free from doubt and to warrant the extraordinary remedy of supplementary injunctive relief. . . . To avoid the appearance of affirming the Court's decree upon the negative quality of a finding that we discern no error in its order, we go further and say, that, having made the law of the case we are presumed to know what it is, and that, applying the law to the

facts, which, on the defendant's motion to dismiss are regarded most favorable to the plaintiff's, we would have made the same disposition of the case had we been sitting in the District Court when the application for a supplementary injunction was made. We are of the opinion therefore that the order or orders of the District Court should be affirmed and the case be proceeded with expeditiously and in a manner consistent with the law."

On May 26, 1920, the Miami company petitioned for leave to file a supplemental bill in the nature of a bill of review. The company took this step on account of the discovery of "an unpublished book in manuscript form," written by Messrs. Sulman and Picard in 1906. This treatise, a copy of which was found in the possession of T. J. Hoover,[10] to whom it had been given by the authors early in 1907, contained evidence tending to show that patent No. 835,120 was limited to a process of concentration in which less than 1% of oil was added to a freely flowing pulp and the mixture subjected to rapid rotary agitation, until the sulphide mineral formed in a froth. It was also the contention of the Miami company that this treatise, entitled "The Theory of Concentration Processes Involving Surface-Tension," disclosed the point to which the art had advanced, as far as known to the patentees, prior to the alleged date of invention, and that this state of the art left nothing open to invention save the single element of the "whipping in" of external air by rapid rotary agitation. It is apparent from the treatise that Messrs. Sulman and Picard knew that froth had been produced in the Potter and Delprat processes without the use of oil, the lifting force being solely the gas generated within the pulp by the action of acid on carbonate minerals; that they were well aware of the fact that Froment had produced froth of the same character, in the same kind of process, with the addition of a proportion of oil so small as only to film the particles of mineral, so that the film, to all intents and purposes, became part and parcel of the particles themselves; that in the Elmore vacuum process the same kind of froth was produced by using a similarly small proportion of

[10] Mr. Hoover's affidavit was published in the *M. & S. P.* of June 19, 1920.

oil, the lifting force being air drawn out of solution by the application of a vacuum; and, further, that the same result could be obtained in a process using the same small proportion of oil by passing a current of air through the pulp in the form of bubbles, as disclosed in the so-called bubble patent, No. 793,808. The treatise indicates that the patentees, at the time (March, 1905) of their supposed invention of the process covered by No. 835,120, were aware of all these facts, which limited their patent, in their own words, as a "mere practical application of the Froment principle," wherein air was introduced into the mass of pulp by whipping in external air by rapid rotary agitation. Thus the argument for the defence comes back again, much reinforced, to the one brought forward in the first trial of the Hyde case in Montana, eight years ago.

The Court denied this petition of the Miami company, but stated: "In so doing, we express no opinion as to the relevancy or competency of the subject-matter of the petition on questions arising on accounting." This apparently indicates the belief of the Court that the whole matter could be settled in the proceeding before the Master or in a new suit begun by an original bill, and that the proper way to introduce this new evidence was not in a re-opening of the original case but in the proceedings on the accounting, which, in the end, of course, will go back to the Court of Appeals or be adjudicated in the course of a new suit under an original bill.

Meanwhile, although seriously impeded by the numerous attempts to cause the investigation into the later milling methods to be removed from the accounting proceedings, the Master has continued to take testimony, but as yet the *prima facie* case on the accounting has not been completed.

Nevada Consolidated.—On September 9, 1919, Minerals Separation North American Corporation and Minerals Separation brought suit against the Nevada Consolidated Copper Co. in the District Court of Maine, southern division, on patent No. 835,120. The defendant, in answering, raises the issue of validity and denies infringement. This case may be heard some time this winter. On February 16, 1920, Minerals Sepa-

ration brought suit against the same mining company on patent 962,678 (the so-called soluble frothing-agent). The defendant again denies validity and infringement. It is expected that this case also will come up for trial during the coming winter.

It is interesting to note that in these Nevada cases the plaintiff is claiming that pine-oil has certain soluble fractions, and that the use of pine-oil constitutes an infringement of both patents, 835,120 and 962,678. It remains to be seen how Minerals Separation will square its present position with the testimony in the Miami case, wherein its expert, Dr. Leibmann, said that pine-oil, for all practical purposes, was insoluble, and it remains also to be seen how Minerals Separation will deal with the Supreme Court's decision in the Butte case where it was held that pine-oil was "an oil having a preferential affinity for metalliferous matter" within the description of patent 835,120. The legal definition of "solubility" will be awaited with interest, likewise the juridical effort to distinguish between the use of the term in chemistry and in metallurgy respectively.

Magma.—On January 10, 1920, the two Minerals Separation companies filed suit against the Magma Copper Company, also in the District Court of Maine, southern division. In this suit the same patents, 835,120 and 962,678, are involved. The defendant denies infringement and questions the validity of the second patent.

In this case, as in the Nevada cases, there will be presented squarely to the Court the question whether or not the Callow or other pneumatic cell is an infringement of either patent. In the mills of both companies the operations have been excluding any prior agitation other than is necessary to mix the oil with the ore, so that the agitation described in these patents, if present, must be found within the pneumatic cell. The decision in these cases ought to settle definitely the validity and the scope of the first patent, both as to the character of the frothing-agents and the meaning of the agitation prescribed in the claims. The validity of the patent for a soluble frothing-agent should be fought to a finish, and it should be ascertained

what is a "soluble frothing-agent" and whether it is covered by the description of the oil of the first patent; and if not, we should be told the meaning of the phrase "agitating the mixture to form a froth."

As yet Minerals Separation has not brought suit against any other of the alleged infringers; the cases now pending raise practically all the important questions left in doubt by the precedent litigations, and while Minerals Separation may find it necessary to bring additional suits to prevent its rights from lapsing by limitation, it would appear certain that the decisions in the several cases pending should determine definitely the extent of the monopoly that Minerals Separation is to be permitted to exercise by law.

TESTING ORES FOR THE FLOTATION PROCESS[1]

By O. C. Ralston and Glenn L. Allen

Introduction.—Although the subject of testing for flotation has been well presented in T. J. Hoover's book on "Concentrating Ores by Flotation," there is need of later information on this timely subject. Much testing has been done in laboratories not connected in any way with the Minerals Separation company, with which Mr. Hoover was formerly associated as metallurgical engineer, and there have been developed methods of investigation that may prove suggestive to many experimenters.

On that account we have compiled data on the subject of testing both from the literature available and from our own experience, as well as from what we have seen in other laboratories. This paper is designed to present the results of this compilation with a critical discussion of the more important methods now in vogue.

On account of the empirical state of the art of flotation a great deal of testing is necessary before large-scale practice can be commenced on any ore; therefore a small laboratory-machine is necessary in which many tests involving many variables can be made in a short time. The machine must be so designed and so operated that a close approximation to the results possible with full-sized flotation machinery will be obtained. In a mill-plant it is a matter of some difficulty to control conditions through a wide range of such variables as temperature, acidity, quantity of oil, percentage of solids in pulp, fineness of grinding, etc., and as the proper treatment of a given ore can be ascertained only through testing it first, a critique of the testing methods in use is in order.

[1] Revised from the *Mining and Scientific Press* of January 1 and 8, 1916.

Many people have had the experience of reading the available literature on flotation testing and of failing to get satisfactory results when the described testing was attempted. To actually witness some good test-work and learn thereby the appearance of froth, the exact manipulation of the machine and froth, goes far toward bringing the beginner to a point where he can test efficiently. None of the literature mentions the fact that it is difficult to get a high percentage of extraction and a high grade of flotation concentrate at the same time. The beginner often strives after both of these things in a single test, whereas he should determine how each can be attained before he attempts to obtain both simultaneously. Furthermore, it is difficult to manipulate a small machine to give as good results as a large one, until after considerable practice. So the small machine is generally pessimistic, compared with the large one. It is practically essential for the beginner to weigh and assay all of his products in order to see if the extraction and the grade of concentrate are satisfactory, where an experienced manipulator can often tell by aid of past experience and the use of a glass or microscope whether he is getting good results or not.

With these points in view, we shall describe first the satisfactory machines and their operation. Then we shall give a more general exposition on what variables to study and what points to observe.

Flotation-test apparatus must necessarily be classified in the same way as large-scale machines, namely, as film-flotation machines, acid-flotation machines, and froth-machines of both pneumatic and mechanically agitated types. Film-flotation, as exemplified in the Macquisten [2] and in the Wood machines, does not seem to have the same wide application as does froth-flotation; hence little need be said about them.

The Wood machine can be built in miniature and for several years a small machine of the type sketched has been used in the plant of the Wood ore-testing works at Denver.[3] This small machine was about two feet long and one foot wide. The method

[2] *M. & S. P.*, Vol. XCVI, page 414 (1908).

[3] H. E. Wood. Trans. A. I. M. E., Vol. XLIV, pp. 684–701 (1912).

of operation is the same as that of the full-sized machine. (See Fig. 1.)

As neither of these machines has been much used in practice, they are merely mentioned for the sake of completeness. Hoover[4]

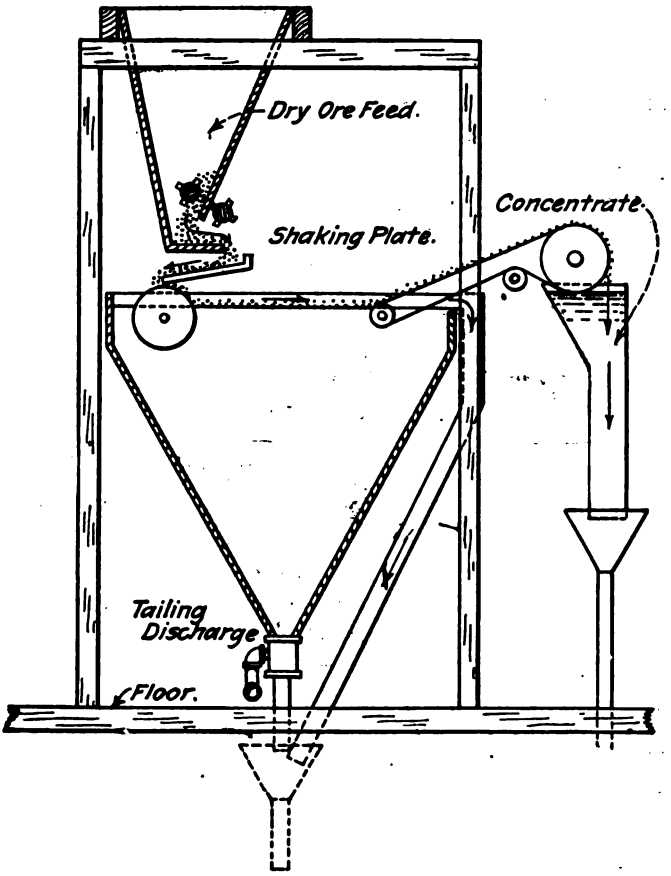


FIG. 1.—The Wood Machine.

has recommended a test on a vanning-plaque, so that the sulphides will float off onto the surface of the water, but we consider this test of practically no value. Hoover, however, acknowledges that it is merely a test illustrative of the film processes.

[4] T. J. Hoover. "Concentrating Ores by Flotation," 1st edition, page 77.

In testing ores for the Potter or the Delprat process, Hoover's text is again the source of information. A 200-c.c. beaker is used with 100 c.c. of 3% H_2SO_4 and brought to nearly boiling temperature. The ore when introduced into this yields a froth composed of sulphides supported by bubbles of CO_2. In case the ore is deficient in carbonate, an addition of as much as 3% of calcite or siderite is made. The froth is skimmed with a spoon as fast as it forms. We have noticed that a great deal of mineral is often lifted partly but never reaches the surface. Consequently extractions are low, although the grade of concentrate

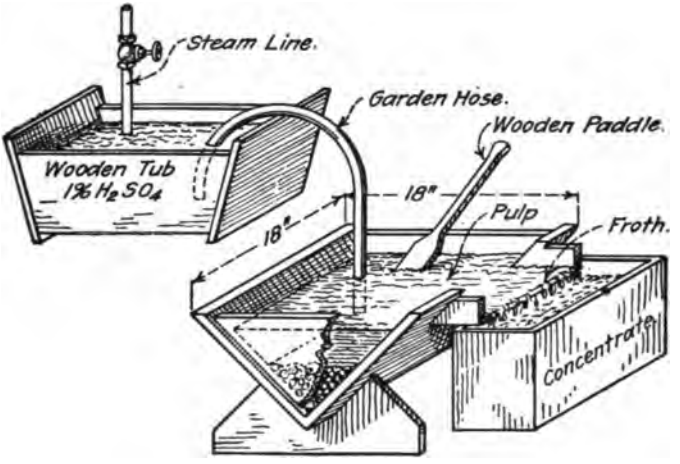


FIG. 2.—A Potter-Delprat Test-Machine.

obtained is often very good. For practical purposes, however, the test is not of much value. A better test-machine is the small unit shown in Fig. 2. The acid should be allowed to run down through a section of garden-hose to within an inch of the surface of the ore and the ore should be kept stirred with a wooden paddle so that the bubbles of CO_2 generated by the action of the acid can lift the sulphides out of the body of the pulp. The froth formed should be skimmed with the paddle as fast as made, then filtered, dried, weighed, and analyzed. Not many ores yield gracefully to this treatment and slimes give poor extractions. Fines and Wilfley-table middlings are better adapted, and the

presence of siderite in the pulp is desirable, as it reacts slowly with dilute acid. From 1 to 3 % H_2SO_4 is best in testing and ½ to 1½% solutions on the large scale will give about the same results. The temperature of the pulp should be maintained at 70° C. by use of a steam jet. Five to ten pounds of ore per test is necessary. The extractions obtained are always lower than in full-sized units. While oil is not necessary in this process it will greatly assist in the flotation, and the addition of a small amount is often of much assistance in test-work.

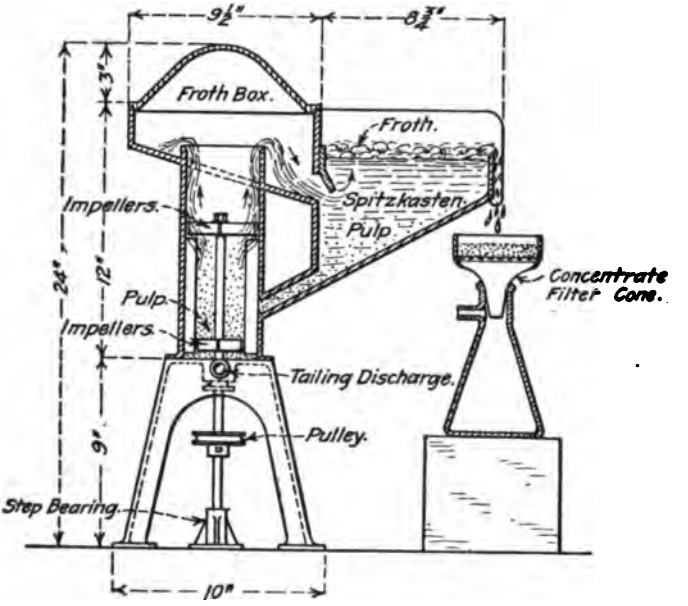


FIG. 3.—The Janney Test-Machine.

Mechanical Frothing as developed by the Minerals Separation company in England and Australia, and modified by many others, has been one of the most important methods of flotation. Therefore the laboratory machinery that has been developed is at as high a state of perfection as any such machinery now in use.

The Janney machine is probably the best designed machine for getting reliable quantitative results on a small quantity of ore. A sketch is appended (Fig. 3). It can be seen that the

agitation compartment is cylindrical in shape and that its top is surrounded by a froth-box, which slopes into a spitzkasten, where the froth can be skimmed. The tailing sinks to a return-hole at the bottom, passing into the agitation-compartment again. To provide good agitation, four vertical baffles are attached to the wall of the agitation-compartment, against which the pulp is swirled by the two impellers. Lining the walls with expanded metal lathing or with a coarse-mesh iron screen adds to the thorough mixing that the pulp must receive. The two impellers are on a common shafting, which enters the machine through a stuffing-box in the bottom of the machine. The lower impeller with four vertical vanes is submerged; it agitates and emulsifies the pulp while the upper impeller, likewise with four vertical vanes, acts as a pump to lift the pulp and beat air into it. A pulley and belt connect the shafting with a variable-speed motor.

A dome-shaped lid is used on the machine. A small hole in the top of the dome allows the introduction of oil, acid, water, or other materials without the removal of the lid. The lid is so constructed that it can be turned upside-down with the dome extending down into the froth-box, and in this position it can act as a funnel. The dome rests then on the top of the agitation-compartment and no froth can escape into the froth-box. This allows a period of agitation of the pulp before the dome-top is turned right-side up to allow aerated pulp to overflow into the froth-box and down into the spitzkasten, where the froth can be removed.

A discharge-plug at the bottom of the machine allows the flushing out of tailing after the test has been completed. So careful has been the design of this test-machine that even this discharge-plug is beveled to fit flush with the bottom of the machine and thus afford no dead space in which the solids might settle.

The spitzkasten is long and narrow, in order to permit a deep froth to be formed and to travel over as long a space as possible, before reaching the discharge. This tends to allow more of the entrained gangue to settle out of the mineral-froth. The sides of the spitzkasten are of heavy plate-glass, each fastened to a

metal-frame by means of screws. The wrought-iron shaft projects through a brass stuffing-box and is supported by a ball-bearing beneath. All the other metal parts are of cast aluminum.

The small variable-speed motor may be of either D. C. or A. C. type. F. G. Janney recommends the use of a General Electric, shunt-wound, direct-current motor, for 230 volts, with a rated speed of 1700 r.p.m. and ¼ hp. The impeller-shaft is to be driven at 1900 r.p.m. maximum speed. For speed-control he recommends a General Electric direct-current field-rheostat, with an ampere capacity of 1.25 to 0.063 at 250 volts.

In our own laboratory it was desirable to use the ordinary city-lighting circuit of 110 volts, A. C. On that account we have found the following motor satisfactory: ¼-hp. General Electric repulsion induction motor, single-phase, 60-cycle, with full speed of 1780 and carrying 4.2 amperes at 110 volts, or 2.1 amperes at 220 volts, depending upon the voltage of the current supplied to the machine, either voltage being acceptable. Speed-control is obtained by the use of an ordinary field-rheostat in series with the motor. Such a motor has a speed varying with the load and with the voltage applied. As the load is practically a constant, the speed will depend upon the amount of resistance in series with the motor. As the majority of laboratories find a city alternating current more convenient to obtain, such a motor is recommended.

The operation of the machine is as follows: It is set up on a bench convenient to the sink and to running water. The motor is set up one foot to the rear with the switch and rheostat placed so that they can be easily reached while standing in front of the machine. A ¼-in. round-leather sewing-machine belt is used for drive. The bearings are well oiled, the stuffing-box is properly packed, and some attention should be given to it occasionally in order to see that it is kept screwed tight enough to avoid leakage.

Enough clear water is run into the machine to barely show in the spitzkasten and the motor is started at its lowest speed. A 500-gm. charge of ore ground to at least 48-mesh is added and the cover placed on the machine in its inverted position. This is done to allow thorough mixing without circulation of the pulp.

All or part of the oil and other reagents are now added and the motor brought up to full speed for 30 seconds. The speed is again lowered to the minimum and the cover is turned over into its upright position. The speed is then raised and water is added through the hole in the top of the lid until the froth in the spitzkasten is nearly at the overflow-lip. The ultimate speed of the agitator will depend somewhat upon the character of this froth, as some oils will give a deep persistent froth, while other froths are thin and brittle and allow of more water being added to the machine, as well as more violent agitation in order to beat more air into the pulp. The froth may either be allowed to flow out of the spitzkasten of its own weight or skimmed with a small wooden paddle. It is a good idea to wet the glass sides of the "spitz" with water while the froth is rising, so that none of the froth will stick to the glass.

The duration of the test is about five minutes with an ore that floats easily, while other ores will require a considerably longer time to allow the entrained gangue to settle out of the froth before it is discharged from the machine. In such cases it is best to hold back the froth until its appearance shows it to be fairly clean. Beginners are likely to dilute their froth with too much gangue. In a large-sized machine the froth can travel over from four to eight feet of spitzkasten before it is discharged, while in this test-machine it only has a travel of about 10 inches. Consequently, the small machine is liable to yield concentrate of too low a tenor. The same applies to most other machines for making tests on flotation.

The concentrate may be caught in a pan or on a filter. After the test the machine is brought back to low speed and the tailing-plug removed, so that the tailing can be caught in a pan or bucket, or run to waste.

If it is so desired, this rough concentrate can be put back into the machine and treated in the same way as the original sample, or the concentrates from several tests combined to give enough material for re-treatment. If this is done three products are made, namely:

A "rougher" tailing, to waste.

A clean concentrate, for shipment.

A "cleaner" tailing or middling, which in actual practice is returned to the head machine.

When these conditions are observed results only slightly lower than those possible with a big machine can be obtained. A test can be run in from 5 to 30 minutes in such a machine with 500 grams of ore in anything from a 3 : 1 to a 5 : 1 pulp. The glass sides of the spitzkasten allow close observation of the condition of the froth, and this is a great advantage to the beginner. The small amount of ore necessary for a test is a matter of considerable convenience, as fine grinding of the ore in the laboratory is often irksome. The aluminum casting is little corroded by either acid or alkaline electrolytes. The return of pulp from the "spitz" to the agitating-compartment allows the material to be treated until all mineral has been removed without stopping the machine, so that a single treatment yields a clean tailing. However, a second treatment of this "rougher-froth" is sometimes necessary in order to get a high-grade concentrate. Clean tailings generally mean only medium-grade concentrates due to entrainment of gangue, in the removal of all the mineral.

The stuffing-box in the bottom will probably leak if not watched. However, this driving of the impellers from below, instead of from above, leaves the top of the machine free for the operator and is more convenient in every way. This is of importance in a laboratory-machine, and will excuse the use of a stuffing-box. In large-scale machines a stuffing-box underneath would not be tolerated, and the drive should be from above. We would also suggest a sheet-lead construction as being more easily built. A $\frac{1}{4}$-inch sheet-lead is sufficiently rigid to stand up well, while it is ductile enough to be worked readily into the desired shape. The joints are easily burned, and it is acid-proof.

The Hoover Machine, Fig 4, was designed after a test-machine described in the second edition of Hoover's book, being copied from one of Lyster's patents, and has been much copied by people wishing to make flotation tests. An improvement over this construction was published by Ralph Smith [5] recently, and a modi-

[5] *E. & M. J.*, Vol. C, page 395 (1915).

fied form of the same is shown in Fig. 5, which is that sold by the Denver Fire Clay Co. under the name of the Case machine, for $75. Either a variable-speed motor is belted to the pulley that drives the stirring mechanism, or a pair of cone-pulleys on a constant-speed motor is used. A less original machine but a fairly useful one is that described in the *Mining and Scientific Press* of April 15, 1916, which is said to be used at the Suan Concession, Korea. All of the dimensions are given in the drawing (Fig. 6) so that it can easily be built. Its capacity is said to be 100 lb. per hour and its total cost, including the motor, is under $50. It is used for checking small-scale tests and occasionally for separating chalcopyrite from scheelite in small lots. This construction has been popular because it can be made of wood, at small expense. The Janney machine will cost about $125, while the

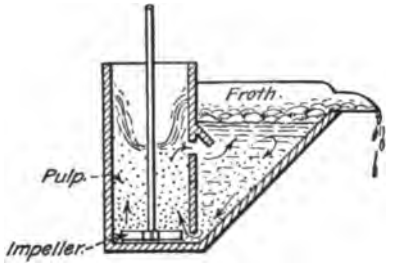


FIG. 4.—Original Form of Hoover Test-Machine.

Hoover machine can be built for a small fraction of that amount. Mr. Hoover's original drawing does not show the spitzkasten drawn to a point, as only the front side was beveled. Our sketch shows both sides beveled. This is desirable, as it eliminates space in which fine sand can settle, and tends to minimize the amount of pulp lying inactive in the spitzkasten. In the agitation-compartment the pulp is swirled into the corners, where it is well mixed with air; hence the baffles sketched in the Janney machine are unnecessary. One objection, however, is that unless the agitation-compartment is very tall the pulp being swirled into the corners has a tendency to splash out, and a lid similar to the one on the Janney machine is desirable. However, it is difficult to attach one because the stirrer-shafting is in the way.

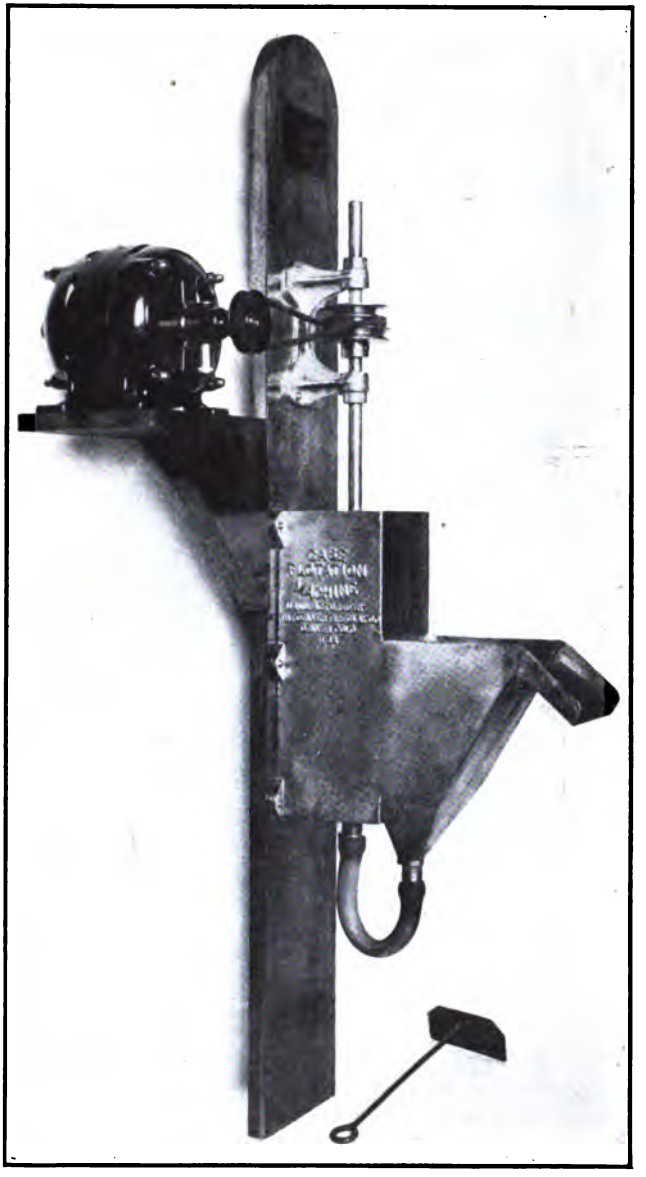


FIG. 5.—The Case Flotation Machine.

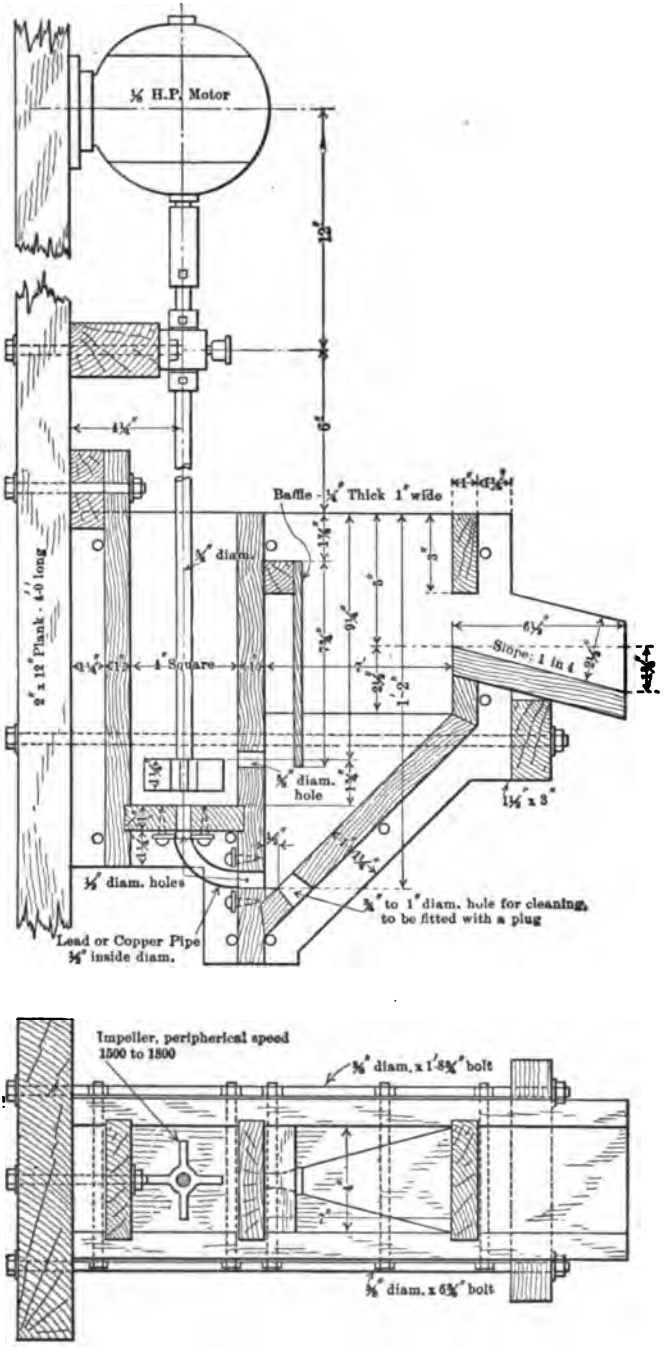

¼ H.P. Motor
12"
6"
4¾"
Baffle - ¼" Thick 1" wide
¾" diam.
9" x 12" Plank - 4'0 long
1" Square
Slope: 1 in 4
⅝" diam. hole
1½" x 3"
½" diam. holes
¾" to 1" diam. hole for cleaning, to be fitted with a plug
Lead or Copper Pipe ½" inside diam.
Impeller, peripherical speed 1500 to 1800
⅝" diam. x 1'8¾" bolt
⅝" diam. x 6¾" bolt

FIG. 6.—Flotation Machine Used at the Suan Concession, Korea.

The operation of this machine is practically the same as that of the Janney, except that without glass sides on the spitzkasten it is hard to get as clean a froth.

A most interesting test-machine is that of Roy & Titcomb,

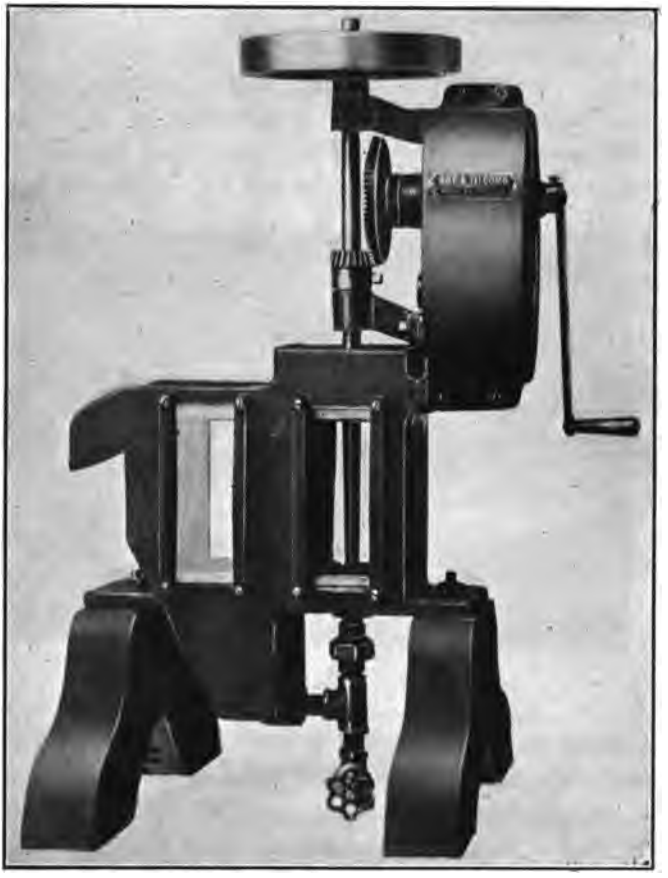


FIG. 7.—Roy & Titcomb Test-Machine.

of Nogales, Arizona, which is run by hand-power by means of gears and a balance-wheel. This machine is shown in Fig. 7. The impeller shaft is suspended on ball-bearings and the cells are cast in one piece. The possibility of taking such a hand-driven

machine into remote localities for test-work is immediately suggested. It costs $85.

The Slide Machine, as shown in Figs. 8 and 9, was designed by Hoover and perfected by many others. In recent practice it is motor-driven. A number of these machines were given by James M. Hyde to various universities in this country. Many people favor this apparatus for the reason that they have had little opportunity to use any other design. In this machine the agitator is driven from below through a stuffing-box, as in the Janney, with the consequent freedom of the top of the machine for the convenience of the operator. The top half of the machine is so

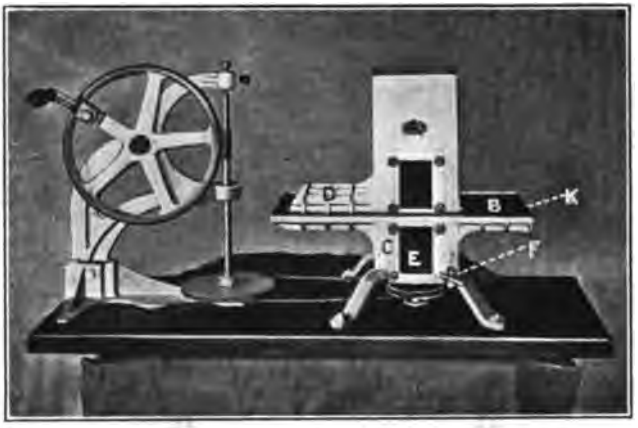
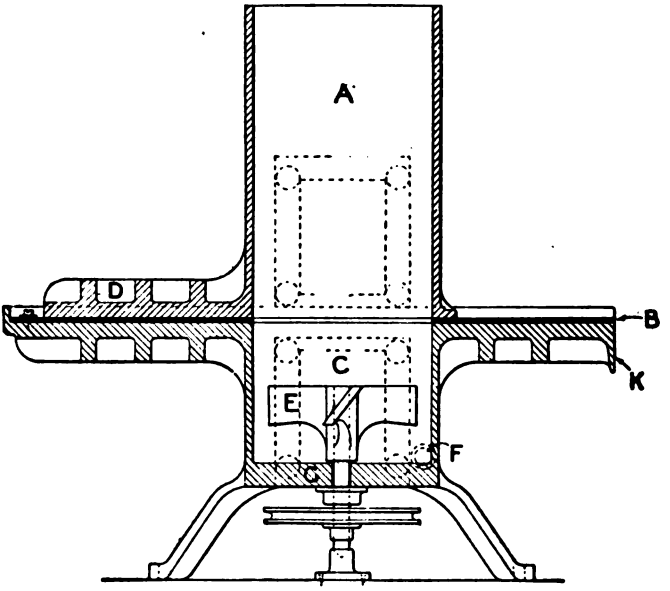


FIG. 8.—The Slide Machine.

constructed that it can be slid to one side, cutting off the froth formed in the agitation from the gangue, which is allowed to settle. The operation consists in agitation with oil and other reagents, then a period of quiet during which the froth collects at the top while the gangue sinks. Two windows in the side enable the observer to see when the gangue has subsided sufficiently to allow the top half to be slid along the rubber gasket, cutting off the froth from the remainder of the pulp. The time necessary for the settling of the gangue is sufficient for much of the gangue to separate from the froth, leaving only clean sulphides in the froth. This element of the machine has made it of some value in

testing flotation-oils, but in a weak froth much of the sulphide mineral also settles out and is lost, so that the test-results with this machine often show unnecessarily low extractions and a high grade of concentrate. On the other hand, when conditions are adjusted to give a froth persistent enough to hold all the sulphide mineral, considerable gangue is entrained in the stiff froth. Further, after skimming one froth we find it necessary to add more water and start the machine again to make more froth.



LONGITUDINAL SECTION.

FIG. 9—The Slide Machine.

It is hard to make the slide machine give a high extraction with only one agitation. The intermittent character of such work and the time necessary to wait while settling are disadvantages that make the Janney or the Hoover machine of greater utility, in our opinion. The parts are of cast aluminum with a rubber gasket between. A charge of 500 to 1000 grams of ore is used.

One other test-machine, designed more recently, is that of Kraut & Kollberg, often referred to as the K. & K. It is a reproduction of the larger machine of the same make (shown on another

page) although it does not do the large machine full justice in the test-work done. It consists of a cylindrical rotating drum covered with longitudinal riffles contained within a cylindrical casing placed on one side of a spitzkasten, into which the agitated pulp is thrown by the motion of the rotating drum. It is adapted to a charge of about 2 lb. or 1000 gm. of ore. It is opened by loosening the hinged top which is held by thumb-screws. A great deal of time is necessary in cleaning out this machine after a test. The tailing can be drained out by pulling a stopper in the bottom. Oil and other reagents are introduced during a test through a small hole in the front. Sand will tend to accumulate, during a test, on the bottom of the machine. Fast and loose pulleys are provided and the speed recommended is 400 r.p.m. The machine is sold by the Braun Corporation of Los Angeles for $75.

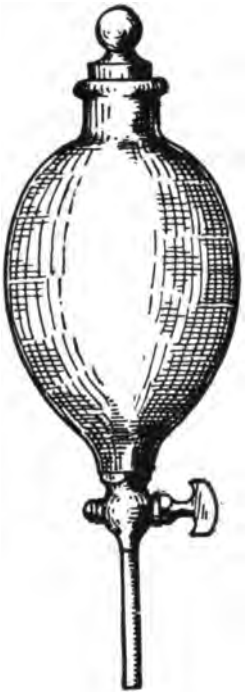


FIG. 10.—Separatory Funnel.

Separatory Funnels.—During the past year an article on practice in Mexico [6] mentioned the fact that much of the preliminary testing on the ore was done in separatory funnels, in which the charges of pulp, oil, etc., were shaken, after which the cock at the bottom of the funnel was opened and the tailing run into a second separatory funnel for further flotation tests, the cock being closed in time to catch the froth. The versatility of experiment shown by the use of such apparatus (Fig. 10) is commendable. Obviously, this arrangement is open to the same objections as is the slide machine, except that separatory funnels are simple and inexpensive.

Elmore Machine.—As far as we know, no small test-machine for the Elmore process has come into common use on account of

[6] *M. & S. P.*, Vol. CXI, page 122 (July 24, 1915).

the fact that the pulp must be lifted through a tube corresponding in length to the column of water equivalent to barometric pressure. This makes an awkward laboratory machine. Mr. Hoover (2d edition, page 98), describes "illustrative" experiments with the pulp in a bottle connected with a water-pump for producing a vacuum, but no quantitative method of this kind has been developed.

Other miscellaneous frothing tests are in the literature but most of them are merely "illustrative." Putting a charge into a soda-water siphon, pumping in air to dissolve in the water, and then releasing the charge into a beaker gives nice-looking froth. In some of the lawsuits square glass candy-jars (Fig. 11) with a motor-driven impeller have been used to show flotation phenomena in court. In a recent U. S. patent (No. 1,155,836) taken out by T. M. Owen, one of the engineers of the Minerals Separation, Ltd., is a sketch of a simple test-machine made of an ordinary 2½-litre acid-bottle. (See Fig. 12.) This corresponds to the sub-aeration type of machine and is recommended by Mr. Owen for test-work when such a type of machine seems necessary, as in differential flotation. Air is led into the pulp through the stopper in the bottom and beaten into the pulp by the impeller. The four large baffles above the impeller prevent the swirling of the pulp from rising through them, so that there is a quiet zone in the top of the machine where the froth can collect. One great beauty of such a machine is that any froth formed will rise immediately to the discharge. However, we believe that the Janney and Hoover machines are the most useful of the mechanically-agitated type.

Pneumatic Flotation.—Among the different pneumatic machines, as far as we are acquainted, the Callow test-machine is the only one of laboratory size that has been much developed. It is merely the commercial Callow machine reduced in size. (See Fig. 13.) Later development in the laboratory of the General Engineering Co., in Salt Lake City, has resulted in the reproduction of the whole plant in miniature, with Pachuca mixer, roughing-cell, cleaning-cell, vacuum-filter, and sand-pump to return middling to the Pachuca mixer. As seen in the drawing, the pulp is mixed well in a Pachuca tank of small size, overflowing

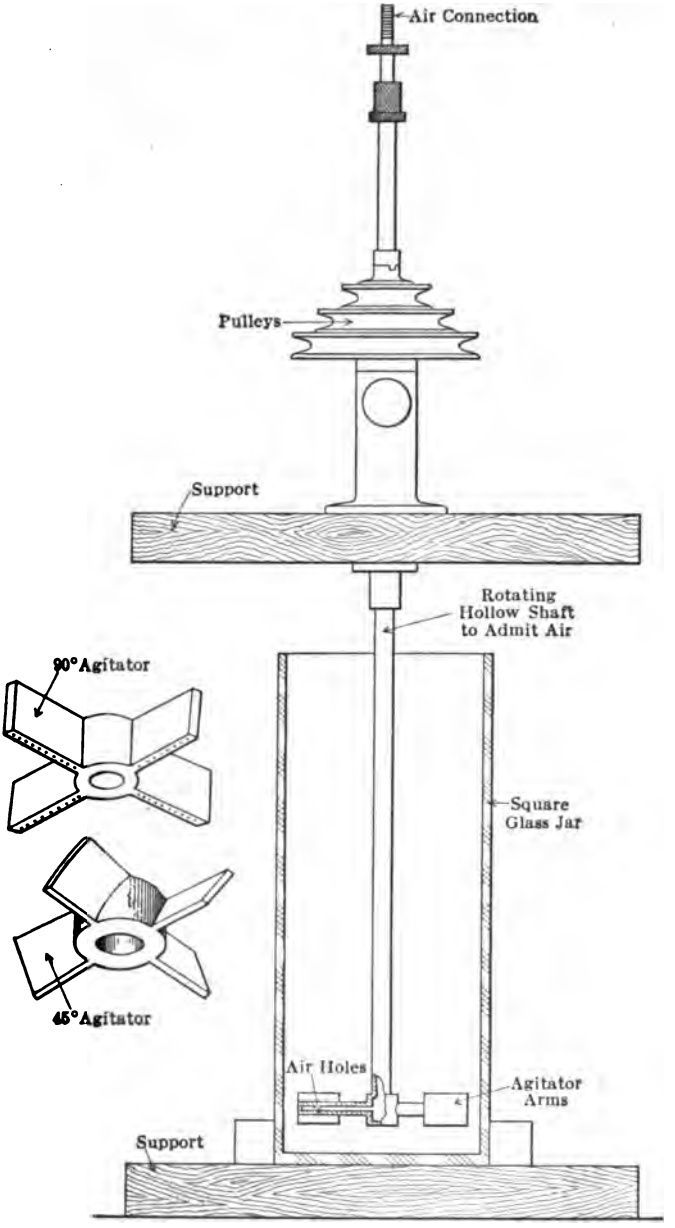


FIG. 11.—The Square Glass Jar Machine.

into the rougher flotation-cell. The tailing from this rougher goes to a sand-pump and is returned to the Pachuca. The froth is treated in a second and smaller pneumatic flotation-unit, giving a concentrate that overflows into an ordinary laboratory

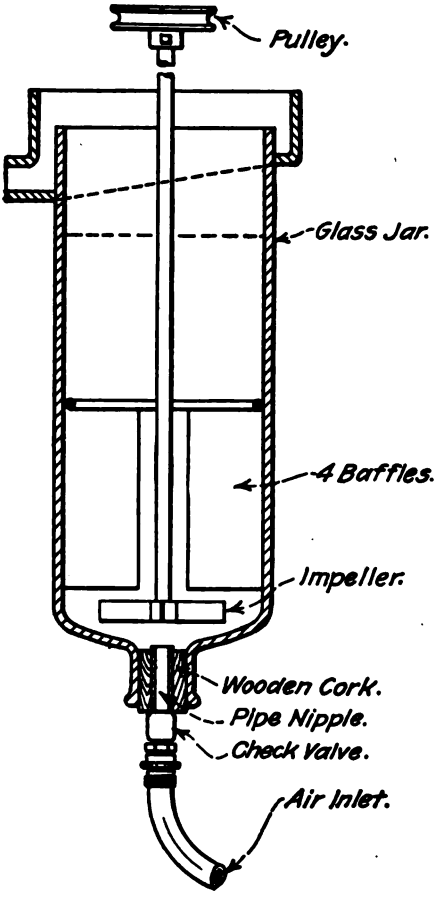


FIG. 12.—Owen Test-Machine.

vacuum-filter actuated by a water or aspirating pump. The tailing from the "cleaner-cell" consists of a middling that likewise flows to the sand-pump and back to the Pachuca.

A novice will have no small difficulty in operating such an installation, as there are a number of things to be kept in opera-

tion at the same time. The mixture of ore, water, oil, and any other reagents is fed either into the suction of the sand-pump or into the top of the Pachuca after air has been started into the various machines. The overflow from the Pachuca into the rougher-cell accumulates until a nice froth is coming up and nearly overflowing. Then the tailing-discharge valve on the rougher is gradually opened and froth allowed to overflow from the cell into the "cleaner-cell." It is best to get most of the charge circulating before much concentrate-froth is allowed to overflow, the overflow of froth being controlled by the main air-valves leading to each unit. After the valves into the individual wind-

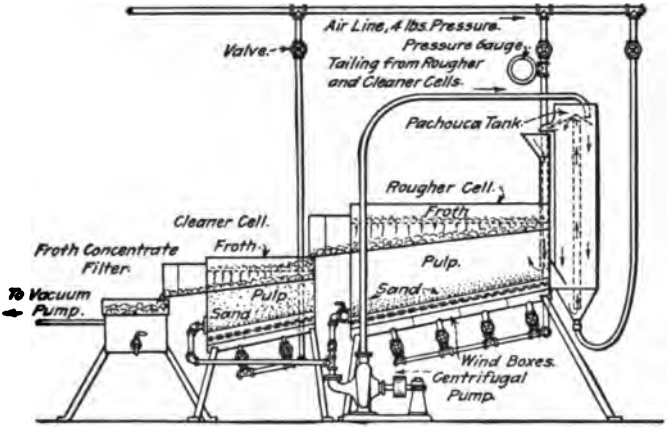


FIG. 13.—Callow Test Set.

boxes beneath the machine have been once adjusted they should never be disturbed, and all control of air supplied should be at the valves in the main pipes. When everything is going well, the air-pressure in the cleaner can be increased until concentrate-froth is overflowing into the vacuum-filter. A wooden paddle to stir any settled material in the flotation cells is of value, as well as a small jet of water from a rubber hose for washing concentrate along the froth-launders and for beating down froth when occasional too-violent rushes of froth from the cells take place. After a test is complete the pulp should be drained completely from all parts of the machine while the air is still blowing, so that solids will not settle in passages or clog the canvas blanket

in the cells. Only practice will allow anyone to get reliable results with this machine. A watch-glass for catching and panning occasional samples of froth is another necessary auxiliary to this equipment. The cost of installing such a set of apparatus is from $100 to $150. At least 1000 grams of ore is required for a test and about 30 minutes to 1 hour is spent. It can be seen that nothing but a finished concentrate and a tailing are obtained. The machine is said to give results closely paralleling those obtained with larger-scale apparatus. A source of supply of compressed air at 3 to 5 lb. per square inch is necessary and the main valves on the air-pipe leading to each machine should be of some type of needle-valve in order to ensure exact control.

Laboratory Manipulations.—Turning from the description of the machines used to the operations on the ore before and after the flotation operation, we have in general the problems of crushing the ore and of drying the froth-concentrate.

As a rule laboratory machinery for the pulverization of ore is of the dry-grinding type, with the exception of small ball-mills that can crush from 1 to 100-lb. charges in the wet. Consequently, most people start with weighed charges of finely ground dry ore, a known quantity of water, of oil, and of acid or alkali. Our experience has been that most dry-ground ore must be treated in an acidified pulp to get good flotation. Doubtless the surfaces of sulphide particles become somewhat oxidized in, or shortly after, dry grinding and the function of the acid would be to clean the slightly oxidized surfaces. Wet grinding usually does not call for so much acid. One interesting experience is that of L. B. Pringle, working on ores from south-east Missouri. He found that drying of a sample of mill-slime before floating in a laboratory machine gave a much higher tailing and a lower-grade lead concentrate. On that account the laboratory samples were kept under water and the proper weight of pulp was obtained for each test by the use of a graduate and a hydrometer, always taking enough of the pulp to get 500 grams of solid. Sulphuric acid did not seem to rectify the oxidation effect obtained in drying because calcium and magnesium carbonates tended to float with the concentrate in the acid pulp.

In nearly all laboratory work finer grinding than is used in practice seems to be necessary. This may possibly be due to the smaller amounts of froth that are formed. Such small quantities of froth cannot form layers as deep as those made in the large machines. If a big particle of sulphide can be entrained with a number of smaller particles, it can be floated, but with a thin froth the chance of such entrainment would seem to be less. Some experimenters have informed us that they were able to float even as large as 30-mesh material, but our own experience is that 60-mesh material is often hard to float with any chance of getting a high extraction, while the operation is performed with much more ease and expedition when the ore is crushed somewhat finer.

Wet grinding is more desirable, as it parallels conditions in practice, where most of the finer grinding of ore is in Chilean, tube, and other mills. However, wet grinding is harder to manipulate in a small laboratory and requires more time. The dry weight of the feed to the flotation machine must be known; hence a weighed charge of dry ore crushed to about 10-mesh can be introduced into a porcelain or iron pebble-mill for grinding and ground for the length of time found necessary to reduce the pulp to sufficient fineness—15 minutes to 24 hours. The charge can then be poured and washed through a coarse screen (to retain the pebbles) into a bucket and thence into the flotation machine. The oxidation of sulphide surfaces is thus avoided, but separate grinding of each charge, in order to know its exact weight, is rather tedious and requires a number of small mills if many tests are being run, on account of slow speed in grinding. A mill with iron balls rather than pebbles is of greater service. It is possible to introduce the flotation-oil before grinding, to be sure that it will be thoroughly mixed. For thick viscous oils this is highly beneficial, as a ball-mill gives about the best conditions for agitation and mixing. Usually 1 to 2-lb. charges are used and a small laboratory mill of the Abbe type serves well, although a good mill can be made with a 10-in. length of 8-in. iron pipe and two heavy iron caps for the same.

Practice in our laboratory has been standardized to a labora-

tory-gyratory breaker crushing to 10-mesh, splitting into weighed samples kept in paper bags and reduced to smaller size by either wet or dry grinding as occasion demands.

A short-stemmed tin funnel about 6 inches in diameter with a one-inch opening is found to be about the most convenient means of pouring a charge of ore into a laboratory flotation machine.

The measuring and testing of flotation-oils in the laboratory has been very inexact in many instances witnessed by us. It is common practice to count the number of drops of oil falling from a small piece of glass tubing. We are using a Mohr pipette of 1 c.c. total capacity for measurement of the amount of oil used in each test. Such a pipette is shown in full size in Fig. 14. It will be seen that this pipette allows measurement of the oil to the nearest 0.01 c.c., which is as close as will ever be desired. If the density of the oil is known, the volume as measured by this method is quickly converted into the weight of oil used.

FIG. 14.

The testing of oil samples for flotative power is a matter that needs standardizing. It is desirable to classify oils according to flotative power, but just how to do this is not exactly clear. A unit of "flotativeness" might be established and each oil referred to that unit in terms of percentage. But it has to be remembered that the best oil for one ore may not prove to be the best oil for another, although two such series of oils might roughly parallel each other. For any given ore, it would be permissible to make such a measurement on a series of oils and group them according to some definite standard. A standard oil might be chosen and the value of a second oil expressed in percentages of the flotative power of the first as determined by using equal quantities of the two oils in tests on an ore under identical conditions. This test could not be fair for the reason that different amounts of two different oils are necessary to accomplish the same results. Further, the conditions of acidity

or alkalinity might favor one oil and handicap another. If we measured the amount of oil necessary to give a fixed percentage of recovery the first of the above objections would be satisfied but conditions of acidity or alkalinity could make the test unfair for some oils. Hence the dilemma as to a standardized test of a flotation-oil.

No single test could definitely place an oil in any scheme of classification and nothing can be done but run a series of tests using varying amounts of the oil to be tested and with varying acidity or alkalinity. The temperature of the pulp must be kept constant although it has a minor effect.

Coutts gives about the only directions on oil-testing that are to be found in the literature of the subject.[7] He states rightly that the first thing to do with an oil is to measure its density, for future calculations, as it will be measured by volume in the laboratory and must later be reduced to weights. He recommends the use of a burette for measuring the oil, but we favor the Mohr pipette mentioned above. He chooses a standard ore on which all tests are to be run and classifies three different kinds of standard tests: (1) for mixed sulphides, (2) differential separation, and (3) flotation of copper and iron sulphides. He states that oils high in phlanderene have proved best for differential separation of zinc-lead sulphide ores. While this is helpful, he does not state just how the oils are to be classified after the tests have been made.

Much work with oils is needed in order to determine if there are any definite constituents in oils that give them flotative power. Research is also needed in the preparation of oils from the wood, coal, and mineral oils in such a manner that they will have maximum efficiency in flotation. Work on this subject has been initiated in our own laboratory and it is known that several of the larger companies have employed oil-chemists to look into such problems. We understand that most excellent work is being done on methods of modifying and reconstructing oils that can be had cheaply. By this we mean more than mere mixing of a good flotation-oil with a cheaper non-selective oil. Sul-

[7] J. Coutts. *E. & M. J.*, Vol. XCIX, page 1079 (1915).

phonating the oils, dissolving them in acids, dissolving modifying substances in the oils, etc., are some of the ideas being tested with varying success. It is on account of all this oil-testing that considerable progress has been made in flotation during the past few years, so that now most of the larger companies are using cheaper oils than they were formerly.

When starting to work with a new ore, there is needed a rapid qualitative method of choosing an oil that seems well adapted to the flotation of the ore in question. Such a scheme is in use in the laboratory of the General Engineering Company in Salt Lake City. Their qualitative tester is designed to test oils for use in the Callow pneumatic flotation-cell and consists of a glass tube of about two inches diameter and two feet long. (Fig. 15.) This can be set on end and closed at the bottom with a one-hole rubber stopper through which passes a glass tube into a small canvas bag. The small bubbles of air coming through the canvas are similar to those used in large-scale machines and can be observed through the glass walls of the tube. With some pulp in the tube, oils, acids, salts, etc., may be added in very short tests until the proper appearance is obtained. An overflow lip is provided in case it is desired to examine the mineral in the froth. A slight adjustment of the air will provide an ample overflow of froth. Two alternative methods of making the bottom of such a cylinder, as published by Alfred T. Fry, of Broken Hill, in the *Mining and Scientific Press* of February 3, 1917, are shown in Fig. 16.

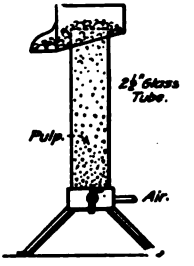


FIG. 15.—Callow Qualitative Tester.

Disposal of the Froth.—The handling of the flotation-froth in the laboratory finds difficulties which are reflected in practice. It is often very slow to settle and filters with difficulty. A vacuum-filter, connected with a laboratory aspirating pump, is a very convenient method of getting the concentrate out of the froth. A large porcelain Buechner funnel fitted into a filtering flask, as shown in Fig. 3, is used at present in our laboratory. A

copper vacuum-filter of much the same type, provided with a porous false bottom of acid-proof wire-cloth, resting on a punched plate, is shown in Fig. 13 of the Callow test set. Filter-papers can be laid over the bottom of either of these funnels to collect the concentrates, and the vacuum beneath sucks out the water and oil of the froth. Such a filter can be placed under the froth-discharge of a flotation machine so that a fairly dry cake of con-

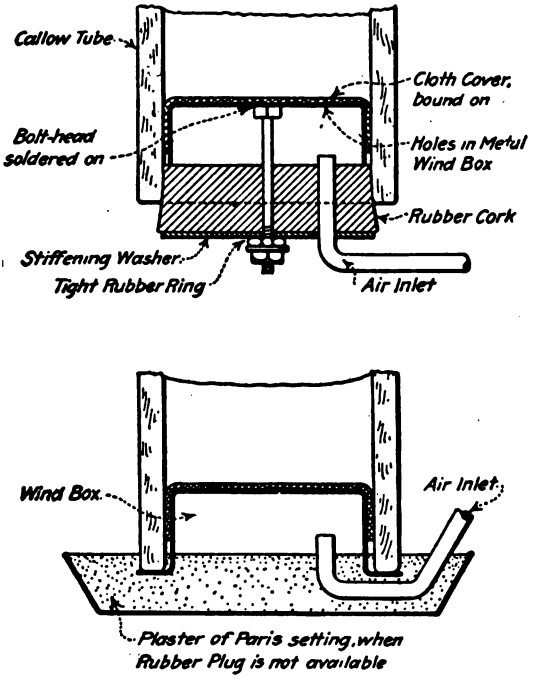


FIG. 16.—Method of Placing Porous Bottom in Oil-Tester.

centrate is ready for further drying at the end of the flotation test. By loosening the outer rim of the filter-paper and then turning the funnel upside down over a pan, the filter-paper with the concentrate can be dropped into the drying-pan by gently blowing into the stem of the funnel. This is set aside in a warm place to dry and later weighed against a filter-paper tare.

If it is desired, the froth can be collected in a glass beaker or other vessel and allowed to stand over-night. A layer of clear

water can then be siphoned off and the thick pulp remaining filtered or dried direct. In some laboratories the froth is dumped onto a shallow pan on a hot plate and the water evaporated. Occasionally such a sample of froth will be left too long, and will be ignited and roasted. We once used a numbered set of shallow pans for such evaporations but prefer filtering before drying the precipitate. A numbered tag is now put in each pan along with the cake.

The products coming from the flotation machine should be watched closely and occasionally panned or examined with the microscope to see what kind of work is being done. This is fairly easy to determine as the sulphides are most of them distinguished easily from the gangue under the miscroscope, and likewise gangue particles in the froth concentrate can often be distinguished. A microscope is a most useful adjunct in a flotation laboratory or mill.

General Considerations.—We have mentioned at various places the relation of the laboratory tests to the large-scale operations and now repeat that in almost every instance the laboratory results are somewhat pessimistic as compared to large-scale work. The reasons are made apparent by the smallness of the machine and the shallower layer of froth often formed under these conditions. Moreover, laboratory operations seem to call for greater amounts of oil, acid, etc., than do the large-scale operations.

Only one of the above machines is adapted to " roughing " and " cleaning " operations in a single test. Present-day practice tends toward re-treatment of at least part of the froth in order to make cleaner and higher-grade concentrates. Consequently, it may be desirable to collect enough froth from a series of tests to be re-treated in a " cleaning " test. Of course, this is provided for in the Callow test set, where only " cleaned " concentrate is discharged from the machine. It is further found desirable to weigh and analyze some of the successive fractions of the froth being discharged from a flotation machine, as the tailing becomes leaner, and determine at what point it may be desirable to re-treat such froth.

Many reports of flotation test-work with mechanical-agitation machines give the speed of the rotation of the agitating-blades. We have found that it was possible to get much the same work done with quite a variation of speeds, the only effect being to lengthen or shorten the time of treatment. We feel that the importance of this matter has been much exaggerated. Some means of speed-control is necessary and the speed can be adjusted in each case until the froth presents the proper appearance as to depth, size of bubbles, color, etc. Speeding toward the end of a test in order to give a deeper froth with a faint line of concentrate on the very top is often advisable. We recommend adjusting the speed in each test to suit the other conditions, rather than running a series of tests with different speeds. Only in the slide machine, where operations of the impeller must be suspended in order to allow froth to collect, is the speed of much importance. Here we recommend agitation for a definite length of time, and then a period of settling. The effect of variation of speed during a definite length of time may be a considerable variation in the amount of froth collected during the quiet period. Hence we are prejudiced against the use of the slide machine except for oil-testing.

When a good set of conditions has been found for the flotation treatment of an ore, it is best to recover the water from each test to see what effect a closed circuit of the mill-water will have. Some oil and chemicals are thus recovered, cutting down the amounts necessary for operation. In fact, a carboy or two of the water to be used in the large mill should be used to make certain that no deleterious contamination will ensue from this source. Under these conditions filtration of the concentrate and tailing for recovery of the water is necessary. Such conditions are provided for in the Callow apparatus above described, and can be applied easily to any of the other machines.

Oil samples for test purposes can be obtained from the various wood-distilling companies now advertising in the technical press, from gas companies and from petroleum-refining companies.

In attacking refractory ores, there are a number of ingenious things that can be done to the pulp both in and out of the ma-

chine. The trouble may be due to deleterious substances, which sometimes can be washed out, rendered harmless by boiling, or by acidifying, or by making alkaline with lime before entering the machine. Occasionally, the ore will not work well under ordinary conditions but will yield beautifully after finer grinding. Sometimes extra reagents are necessary, such as powdered charcoal, modified oil, argol, soap, calcium sulphate, alum, etc. A rational method of devising the proper tests in such cases must be based on some theory of flotation. Colloid chemistry is a branch of knowledge that we believe to be very necessary for such work, as it has facilitated a more intelligent control of our tests and has given wonderful results in a number of instances.

Finally, it is well to be prodigal in the amount of analytical work connected with flotation testing in order to discover interesting differences in gangue-constituents carried into the concentrate, as well as to find the best conditions for leaving out some gangue constituent that is less desirable than the rest. If an experimenter does his own analytical work he can be expected to spend three-fourths of his time analyzing what has been done during the other fourth.

TESTING ORES FOR FLOTATION[1]

By James M. Hyde

The factors involved in the concentration of ores by flotation are so few in number and so readily applied in a small way that it is possible to gain a fairly accurate idea as to the character of the concentrate that may be obtained by flotation, and even the total percentage of recovery that may be made by this process, by means of simple apparatus and small quantities of ore.

It may be the purpose of the testing to determine the character and value per ton of the concentrate that will be yielded if all the metalliferous constituents of the ore are recovered as a single product; to determine the percentage of recovery of the metals that may be won by the concentration; or to recover one or more of the metalliferous constituents of the ore in a concentrate separate from the others. This last—selective flotation—is capable of a degree of development requiring very careful selection of the flotative and modifying agents to be used, and will not be discussed at this time.

The recovery of the metalliferous constituents of the ore in a single concentrate is not a very difficult task if the ore is amenable to treatment by flotation, and any test by which the operator wishes to determine the general characteristics of the concentrate to be produced or the total recovery possible by floating all the floatable contents of the ore together may be made with some kind of standard mixture of oils and tars that will be generally applicable. Various oil-mixtures have been used for this purpose by different operators. I have found that a mixture of three parts Pensacola Tar & Turpentine Co.'s No. 400 pine-creosote or its equivalent, three parts of carbolic creosote, and one part

[1] From the *Mining and Scientific Press* of October 2, 1920.

of crude coal-tar or pitch, makes a satisfactory combination for general testing purposes. For pyrite alone, the No. 400 pine-creosote is usually satisfactory. Others have found crude pine-oil plus 10 to 25% of crude coal-tar satisfactory.

The simplest apparatus for testing ores by flotation is a good-sized clear-glass bottle. A quart-bottle will do very well for 100-gm. samples of ore. An ordinary acid-bottle, such as those in which acids are sold, may be used on samples up to 500 grams. To carry out the test, the bottle should be washed clean and half-filled with the crushed ore and water in the proportion of one part by weight of ore to from two and a half to four parts of water; using a quart-bottle, a pint of water and 200 gm. of ore may be used and the test may be started with five or six drops of oil; using an acid-bottle, half a bottle of water and 500 gm. of ore make a good charge, and from six to twelve drops of oil are used at the start. After the oil is added to the pulp, the bottle should be shaken violently with an up-and-down or horizontal movement and brought to a stop in a vertical position, using care to leave pulp as free from rotary motion as possible. If the ore is especially adapted to flotation and the correct amount and kind of oil have been used, a considerable portion of the metalliferous constituents should rise to the top of the pulp as a froth. After the slime has settled this froth may be removed by carefully raising the water-level in the bottle by adding water through a funnel, the lower end of which is below the water-level, or by pouring water carefully down the neck of the bottle. The sides of the interior of the bottle should be wetted first by pouring clear water slowly into the neck of the bottle. After the froth has overflowed completely the bottle may be permitted to stand until the pulp is settled sufficiently so that the excess water may be siphoned off, and the operation may be repeated with or without the addition of further amounts of oil. This operation may be repeated until it yields no more froth. The bottle-test may be repeated upon an ore, using one oil after another, upon separate portions of the ore, until an oil or mixture is obtained that gives the best results. This test is helpful in selecting the proper oil-mixture to use in a mill, or for trial in more elaborate

tests. It is also helpful in the field or in the mill, for arriving quickly at a qualitative test which will indicate the nature of the concentrate that may be obtained from any particular ore.

FIG. 1.—Pneumatic Test Equipment. Flotation Machine, Reduction Valve, Filters, and Drying-Oven.

As a qualitative test it may be of great value in the hands of the mill-foreman or shift-boss in testing the tailings from flotation machines or from vanners and tables, and in testing the overflow from de-watering devices, to see how much fine sulphide

they contain. I have found this test very useful around plants. No equipment is needed other than a clear-glass quart-bottle and a bottle of the oil or oil-mixture that has been found suitable for the ore, this bottle being equipped with a good drop-stopper. The type of bottle used for Welch's grapejuice, because of its shape and size, is particularly useful for collecting samples to be tested and for overflowing the concentrate most completely and quickly.

The bottle-test may be made to yield quick quantitative results of fairly reliable kind if it is manipulated skilfully, repeated agitation being used until no further concentrate is produced. A simple method of expediting the work is to take an india-rubber sack or "balloon," such as is made for the whistles that delight children. If one of these, attached to the end of a glass tube, is introduced into the bottle after the agitation has taken place, water may be introduced into the sack through the tube and the water-level raised so that the concentrate overflows without the pulp being diluted. The rubber sack may then be emptied by siphoning and removed from the bottle, and the operation may be repeated with the minimum loss of time. If a rubber bag is not available, a sheep's or pig's bladder might serve as a satisfactory substitute.

On certain ores a modification of the bottle-test may be carried out effectively where the desired result is not a process to be used in practice but to get a quick idea of what kind of concentrate the metalliferous constituents of the ore will yield when separated from the gangue. The manipulation is as follows:

To the pulp in the bottle may be added from 1 to 10% of limestone, ground sufficiently to pass an 80-mesh screen. The oiling and the agitation may be carried on as before. A sufficient amount of sulphuric acid may now be added to start the generation of carbon di-oxide in the pulp, and the bottle may be filled with water so that the froth as it rises will overflow into the pan in which the bottle is set. By keeping the pulp stirred with a long rod or tube the sulphides may be completely removed by flotation, if the proper amount of the oil best adapted to the work is used. This manipulation requires some skill and is not recom-

mended for general use; but, like the other bottle-test, it may be advantageous if no other equipment is at hand than that with which the bottle-test can be made. If the pulp is heated, or if the amount of sulphuric acid added is too large, the gas may be generated so rapidly as to expel the pulp from the bottle. For

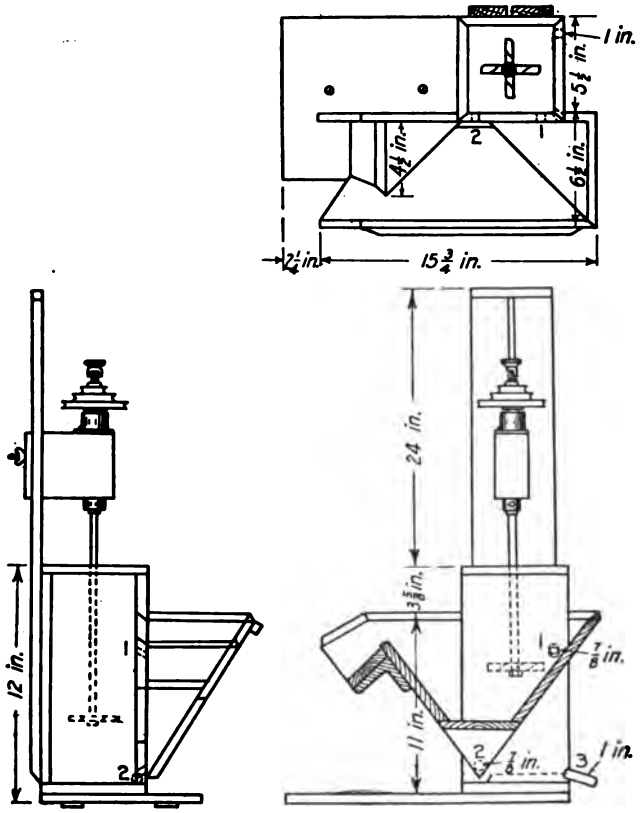


FIG. 2.—Details of Machine for Agitation Test.

this reason, the acid should be added carefully, and with stirring, so that the generation of gas will be kept within bounds. The acid may be added before the agitation takes place if sufficient care be used, in which case the test may be completed more quickly than by any other means, as it may be possible to raise the concentrate completely at one time; but this is not recom-

mended generally because the generation of gas may be so rapid as to throw the acid pulp out of the bottle onto the operator.

In carrying out any test in which acid is used in the presence of a carbonate, the mouth of the bottle should always be pointed away from the operator.

For making flotation tests by mechanical means, a simple apparatus will give reliable results with either the agitation or the pneumatic process. Many types of apparatus have been used and described in the technical press, but the two described herein are so simple and have yielded such satisfactory results that I have come to rely upon them exclusively in my own work.

The machine for carrying out the froth-agitation flotation process consists of a rectangular box in which agitation takes place, and a pointed box in which the froth separates from the rest of the pulp. By reference to Fig. 2 the details of this machine will be apparent. The pulp is kept in continuous agitation and continuous circulation from the agitation chamber through an opening (1) into the separation chamber or spitzkasten from which it returns to the agitation chamber through the opening marked (2). The impeller has blades set at an angle of 45° from the vertical, and is placed about half-way between openings (1) and (2). The impeller is adjustable as to height and may be raised so high that the agitation chamber is completely open for inspection or cleaning. Ordinarily the impeller is adjusted until the best position is found and then left at that position.

The method of procedure in making a test with this machine is to close the opening (1) with a cork, introduce water up to a point just below this opening, and start the impeller. The dry ore is now added and mixed thoroughly with the water, water being added until the level in the separation chamber is about half an inch below the height of the overflow lip. The oil or oily mixture to be tested is added in the proper amount. Where a 500-gm. charge is used the initial addition of oil need not be more than from six to ten drops, unless previous testing has shown that as much as ten or fifteen drops are needed. The oil is added most conveniently by means of a 1-c.c. pipette graduated to

a jet to be applied to the floor of the agitation chamber in such a way as to wash the sand to the discharge opening with the use of the minimum amount of water. After the machine has been cleaned thoroughly the concentrate may, if desirable, be returned to the machine and re-floated in order to raise its grade, the tailing from this operation forming a middling product, which normally would go back into the tube-mill or other fine grinder, to be re-ground and returned to the flotation machine with the regular feed.

This machine is a slight modification of others that have been described previously, its chief individual merit being that it is driven from overhead, the height of the impeller is adjustable, and the settling-chamber is adequate, and is so arranged that the pulp circulates thoroughly without the use of any piping. The impeller in a machine of this type should be driven at a speed of 800 to 1600 revolutions; 1200 is usually about right. A motor of $\frac{1}{8}$ or $\frac{1}{6}$ horse-power is sufficient for use with this imachne.

The pneumatic machine shown in Fig. 3 is useful and can be constructed cheaply. It consists essentially of a wooden base into which is sunk a recess, to be used as an air-pocket into which air is introduced from some simple blower through a gas-cock and short nipple. Over the air-pocket in this base is placed, first, a square rubber gasket, then two thicknesses of 10-oz. duck or its equivalent, then a square of ordinary metallic door-screen, and a second rubber gasket, above which is mounted a square metallic cylinder open at each end having a flange at the bottom as indicated and a basin at the top to receive the concentrate as it overflows, this basin being equipped with a spout by which the concentrate as it overflows is directed into the collecting-basin. That portion of the edge of the canvas which goes under the flange may be saturated with asphalt, care being taken that it does not permeate the portion of the canvas going under the inner portion of the cylinder. The cylinder is attached to the wooden base by a number of screws, and is screwed down in place so tightly that no air or water will escape through the edge of the canvas. The flange, which is made by bending up pieces of the sides, should be reinforced by a square with the centre cut out.

A test is performed in this apparatus as follows:

Five hundred grams of ore is mixed with 1250 to 1500 c.c. of water in an acid-bottle, which is shaken to wet the ore and make a homogeneous pulp. To this is then added from 6 to 15

FIG. 4.—Agitation Machine at Work.

drops of the oil or oil mixture to be used in the test. The pulp is shaken vigorously until the oil is well mixed with the whole of the charge, as previously described in the bottle-test. The oiled pulp is now poured into the cylinder, the air is turned on and carefully regulated by the gas-cock so that the overflow of the concentrate will take place gently. This froth is overflowed until

all of the concentrate the sample will yield has been produced. The tailing may be removed from the machine by tipping it up on the end of the base away from the air-intake while the air is still turned on, and washing out the contents with a jet of water.

FIG. 5.—Apparatus for Pneumatic Flotation. The Author at Work.

The concentrate may be returned to the machine and re-floated as in the test with the agitation apparatus.

The pneumatic machine is dependent upon compressed air from some source. A small mechanical blower, such as the Crowell blower shown in Fig. 6, is useful for this purpose. Such a blower should be equipped with a pop-valve, which may be set

for any desired pressure by adding or removing weights. Figs. 1, 4, and 5 show the machines described, as installed in a temporary laboratory in the Bureau of Mines experiment station at the University of California while war mineral-investigations were being conducted. Air under about 40-lb. pressure was furnished in this instance with a reducing-valve that brought the pressure down to from 2 to 5 lb. pressure.

In some ores pyrite is of little or no value, and it is often desirable to float other sulphides without floating the pyrite. Ordinarily, pyrite is tougher than the other sulphides, and it may be possible to determine a degree of crushing that will leave at least a portion of the pyrite too coarse to float, while practically all of the chalcopyrite or other sulphide that it is desired to save may be fine enough for successful flotation. If it is desirable to leave part of the pyrite unfloated, a test may be made upon ore crushed so that it will all pass through a 30 to 50-mesh screen. Ordinarily, where it is desirable to float all the sulphide constituents of an ore, the whole sample should be crushed so that it will pass through a 60-mesh screen. Even 100-mesh or finer gives the best results in most cases, especially for the bottle-tests.

FIG. 6.—The Crowell Blower.

In testing an ore for the purpose of working out the details of milling practice, the tests should be made upon samples crushed to different degrees of fineness in order to determine how fine it is necessary to crush to get the maximum recovery, and whether or not a finer degree of crushing is necessary in order to get the highest grade of concentrate possible. Screen-analyses should be made on the tailings from these tests.

The usual oils or oil mixtures used in flotation work include turpentine, crude or refined; steam-distilled pine-oil, and the whole range of products recovered by the destructive distillation of pine-wood, falling generally under the head of pine-creo-

sotes and pine-tars; the creosotes and tars produced in the destructive distillation of hardwoods; the neutral and acid creosotes, and refined and crude tars produced in the destructive distillation of coal; and certain crude oils and petroleum distillation products. Qualitative tests may often be made with salad-oil, if nothing better is at hand. Small amounts of pine-creosotes and tars, hardwood-creosotes and tars, coal-creosotes and tars, may at a pinch be made by distilling pitch-pine, oak, maple, alder, etc., or coal-tar, in some simple retort.

The simple mechanical apparatus described herein will give satisfactory and reliable tests, but much of importance can be learned by the bottle-tests, and they may be constantly used to advantage around an operating mill.

The agitation and the pneumatic machines described herein are entirely adequate for making elaborate studies of flotation problems, changing all factors, such as kind and amount of oil, dilution of pulp, fineness of ore, the use of additional reagents, such as lime, ferrous sulphate, copper sulphate, sodium hydroxide, sodium sulphide, and sodium silicate. Where ore is to be ground dry and many tests are to be made, a quantity of the ore should be mixed thoroughly after grinding and screening, and portions of the pulp to be tested should be weighed out into a number of paper sacks to facilitate rapid work. Some ores do not float readily if they have been dried; so, in checking mill-work, the drying of ores and the grinding of them dry should be avoided.

Large Buechner filters, with filter-pumps attached, may be used where many samples are being handled. Where few samples are being handled and assays do not have to be made promptly a wick filter may be used satisfactorily. A single paper towel folded to about an inch wide and flattened with the end held by a wire paper-fastener may be wetted and one end put in the pan of concentrate, the other end being folded over the edge of the pan and brought down below the bottom of the pan. Capillarity will remove the water at a surprising rate. With one paper towel I have taken off over 800 c.c. of water in 24 hours. If the pan is set on the edge of a sink, the water may be allowed to go to waste as it is removed or it can be caught in a pan. When the

sample is air-dry the concentrate on the wick filter may be brushed off. I have found this simple device very useful in removing water from samples of mill-pulp containing slime. Such a sample may be decanted after a reasonable length of time if a pinch of alum is added to it when it is collected. After all the water that can be safely removed is poured off, a further amount may be taken off with a wick filter and the pulp brought to a thick consistence ready to go into a steam-dryer or to be used for flotation tests. A large lamp-wick or a piece of cotton cloth rolled into a wick works well. The paper towel is particularly effective.

A cheap continuous machine of the pneumatic type can be constructed with a tank of wood or galvanized iron, the air-cells being carved out of a straight grained piece of redwood or pine timber. I have constructed such a machine according to the measurements shown in Fig. 7 and 8 and have found it to be very useful in testing under mill conditions. The measurements given may be varied as desired. A machine 4 ft. long and 6 in. wide with two square feet of canvas surface was built some years ago for a total cost of less than $50.

This type of flotation machine was described in the *Mining and Scientific Press* of August 5, 1916, and the following description is quoted with modifications from that article. See Figs. 7 and 8.

The body of the machine is a rectangular tank with a sloping bottom or false bottom, and overflow sides. One overflow side will do for testing. Pulp from the launder (1) enters the feed-chamber (2) and flows into the flotation-chamber, where it passes over the wooden air-cells (4), through the upper canvas surface of which compressed air is being forced. The air is supplied through the hose (5) from the header-pipe (6). Each air-cell is regulated independently by a valve (7). The air rising through the previously oiled pulp builds up a bed of mineral-bearing froth above the water-level; this froth flows continuously over the lip (8) and is carried away by the launder (9). The bed of fragile froth, which readily breaks down unless air is constantly bubbling up beneath it, is prevented from flowing over the tailing-

discharge, where no air is rising, by a partition (10) that divides a dead-water space (11) from the frothing-chamber. The bulk

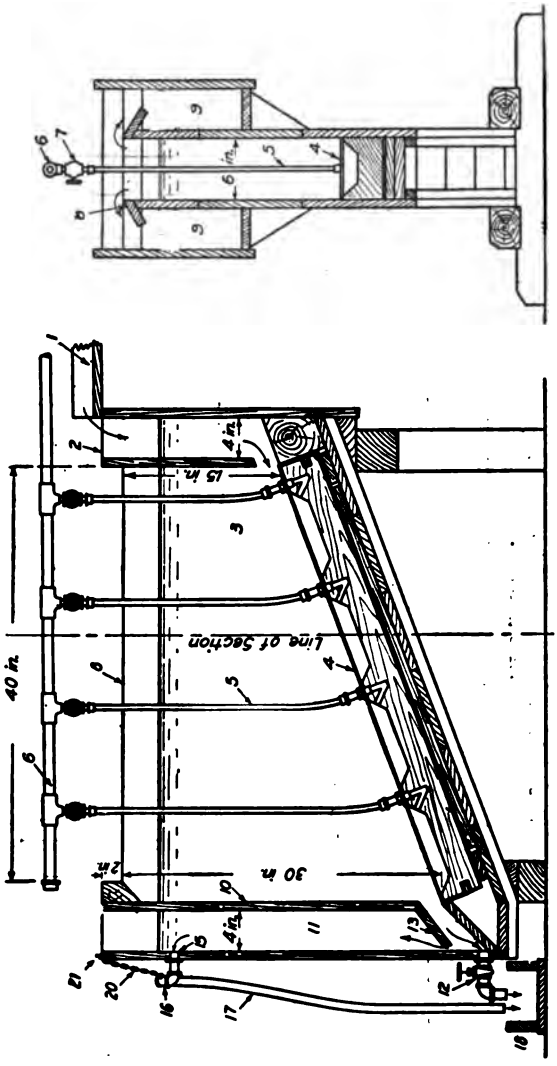


FIG. 7.—Pneumatic Machine for Continuous Testing.

of the tailing is discharged through the valve (12). The deflector (13) guides any bubbles carried toward the tailing-valve by the flow of the pulp back into the frothing-chamber. The deflector

(14) causes a counter-current of froth to flow toward the feed-end of the machine. Slime-tailing flows through the opening

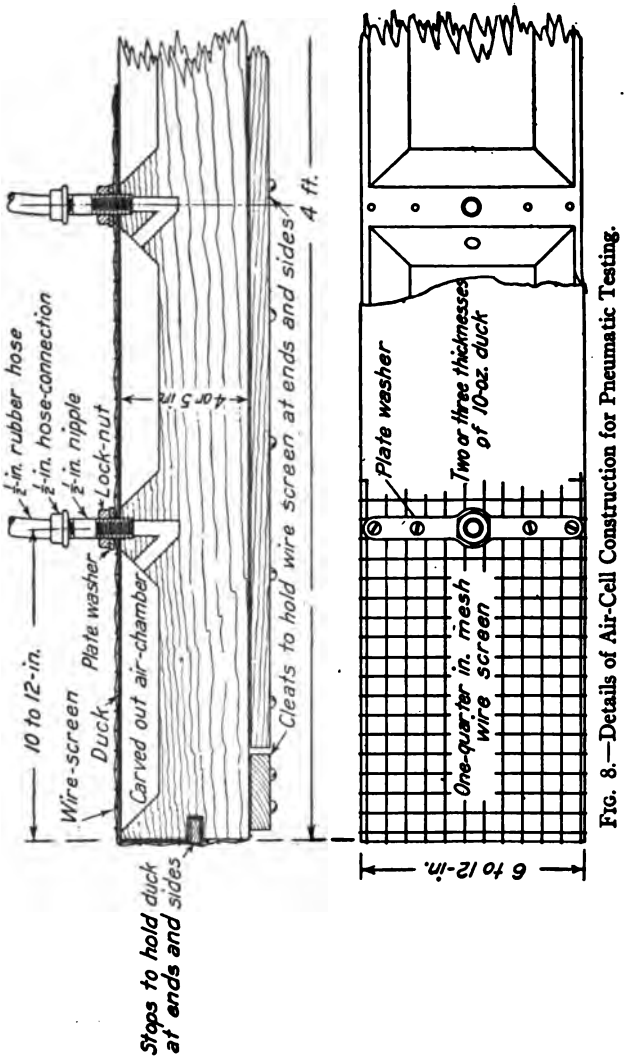


FIG. 8.—Details of Air-Cell Construction for Pneumatic Testing.

(15) and the swing-pipe (16) and through the hose (17) and joins the sand-tailing in the main tailing-launder (18). The swing-pipe (16) may be fastened at any desired height by engag-

FLOTATION IN A MEXICAN MILL[1]

By R. T. Mishler

Present Concentrating Methods.—The mill receives 200 tons per day of crude mine-ore. After being crushed to 2-inch size, this ore is passed over a picking-belt, where 1 ton of high-grade ore and 4 tons of waste are removed each day. The remaining 195 tons of second-class ore is crushed in stamp-batteries, to pass a 4-mesh screen. Lime-water, in the proportion of 7 of water to 1 of ore, is added in the battery. The pulp from these is classified roughly, the coarse sand being ground in a Hardinge mill to pass a 20-mesh screen. The pulp is again classified roughly into four sizes of sand and one size of slime. The sand is concentrated on Wilfley tables and the slime (after being settled to 7 : 1 in cone-bottom tanks) is concentrated on Deister tables.

The slime-tailing, from the Deister tables, is re-concentrated on vanners. The tailing from the vanners settles to $3\frac{1}{2}$ tons of water per ton of slime; the water being further reduced to $\frac{3}{4}$: 1 in a vacuum-filter. The filter-cake is washed with weak barren solution before being sent to the cyanide plant.

The sand-tailing from the Wilfley tables of the stamp-mill is classified carefully in mechanical classifiers; the slime under-size joins the slime-tailing from the re-concentrating vanners, and the sand (after the addition of cyanide solution) enters the tube-mill circuit, where it is joined by 50 tons per day of dump-tailing. All tube-milling is done in cyanide solution. After passing through the tube-mills, the combined current and dump sands are re-concentrated on Wilfley tables. The tailing from these tables is classified, the coarse sand re-entering the tube-mill circuit and the slimed sand being thickened in three 24-ft. Dorr vats before entering the cyanide plant.

[1] From the *Mining and Scientific Press* of July 24, 1915.

METALLURGICAL RESULTS OF PRESENT METHODS

	Gold, oz.	Silver, oz.	Copper, %	Lead, %
The feed to the stamp-mill assays.....	0.1	35.4	0.25	0.7
The concentrate assays.....	2.0	570.0	2.0	10.0
The tailing, after concentration, assays....	0.03	18.0	0.15	0.4

The recovery therefore is: gold, 65; silver, 48; copper, 35; and lead, 45%.

Necessity for Better Concentration.—The above data show that a little more than half the gold is being recovered in concentration, and that the recovery on silver, lead, and copper is less than half the contents in the original ore.

Tests indicate that more than 90% of the metal in the original ore occurs in the form of sulphides. Hence half of the metallic sulphides of the original ore enters the cyanide plant. This is undesirable for the following reasons:

1. The extraction of silver from sulphide metals is poor in the cyanide plant; the concentrate produced from panning current residue assays between 50 and 100 oz. silver per ton, and the tailing from panning invariably assays below 2 oz., even when the residue assays as high as 5 oz.; showing that the poor extraction is due to undissolved silver in the sulphides.

2. The presence of metallic sulphides increases the cyanide consumption. The chemical consumption of cyanide is reduced from 4 to 1 lb. per ton when the metallic sulphides are removed from the heading to the cyanide plant. The present excessive cyanide consumption is due almost entirely to the solution of copper from the ore.

3. The presence of copper and zinc sulphides in the cyanide pulp fouls the solution, thus decreasing the extraction from the rest of the ore.

The possibility of improving results by better concentration of the ore has long been recognized. For this reason, arrangements were made for re-concentrating. Both arrangements have

effected a reduction of assay-value in the final residue and a corresponding increase of profit.

Methods for Improving Present Concentration.—Lately, extensive tests have been made to determine the possibility of still closer concentration. Careful panning reduces the average feed to the cyanide plant from 18 oz. silver to 10 oz. per ton.

Canvas tables give slightly poorer results. A full-sized canvas table, treating tailing from the Deister tables (assaying 20 oz. per ton) produced 15 oz. tailing—an extraction of 25%. Further tests along this line were discontinued on account of securing much better results from laboratory flotation tests.

Laboratory Flotation Tests.—All flotation tests, made in the laboratory, were run in separatory funnels. The general procedure in the tests was to mix 100 grams of *minus* 200-mesh ore with water in proportion of four of water to one of ore. Suitable amounts of oil were then added and the mixture shaken violently. After allowing the pulp to settle for a few moments, the bottom cock of the funnel was opened and the tailing run into a second separatory funnel for another flotation treatment; the cock being closed before the froth began to run out. This process was repeated, on the tailing, from five to seven times. Several hundred tests have been run, all possible variations of conditions being tried. The results of the tests led to the following conclusions:

1. All ores from the mine may be treated by flotation. Semi-oxidized ore from one level yields a tailing assaying 10 oz. silver per ton, while the oxidized ore from another level gives a tailing containing only 2 oz. per ton. The tailing from average ore, when conditions for flotation are right, is 4.5 oz. silver per ton.

2. The grade of tailing appears to be independent of whether the original ore is treated by flotation, or whether wet concentration precedes flotation.

3. The alkalinity during flotation must be between 0.01 and 0.05 lb. per ton of solution. The best results are secured when the alkalinity is 0.025 lb. When the alkalinity is too low, the extraction is poor although the concentrate is clean. When the alkalinity is too high, both the extraction and grade of concentrate

are poor. When the alkalinity is right (0.025 lb.) both the extraction and grade of concentrate are best. The maintenance of proper alkalinity will require the most care of anything in the plant; although it will not be more difficult than the maintenance of proper cyanide strength in the cyanide plant.

4. The dilution may range between 3½ : 1 and 7 : 1; with the best results, on average ore, between 4 : 1 and 6 : 1. When the pulp is sandy a low dilution is best: pure sand, ground to 200-mesh, requires a dilution of 1 : 1. Average slime, like the Deister feed, on the other hand, requires a dilution of 8 : 1. Good extraction may be secured on either sand or slime, provided approximately the proper dilutions are secured in each case. Proper dilutions will be easy to maintain in the plant, for the range for the best work is comparatively large; and when either an excess of sand or an excess of slime occurs in the ore, the proper dilution will automatically adjust itself; for the sand of itself will settle to a thick pulp, while the slime will not settle well, but will remain thin.

5. The temperature is not a matter of vital interest. The extraction is slightly better and the grade of concentrate considerably higher when the temperature is over 100° F., but good results have been secured with the temperature as low as 40° F. It will not be necessary to arrange for heating the pulp, especially at the start.

6. Fine grinding is necessary for good results in flotation. When the mill-heading was crushed to 60-mesh, the tailing from flotation assayed 0.08 oz. gold, and 11 oz. silver; when the same ore was crushed to 100-mesh, the tailing assayed 0.04 oz. gold and 5 oz. silver; and when the crushing was carried to 200-mesh, the tailing assayed 0.02 oz. gold and 3.75 oz. silver.

7. The best flotation agents, so far tested, are pine-oils. Low-grade pine-oil gave as good results as the higher-grade varieties. S. S. pine-oil, of the General Naval Stores Co. (cost 26c. per gal., f.o.b. factory) has given exceptionally good results. For the best work in flotation it is necessary to have this oil present to the extent of 0.6 lb. per ton of ore. In actual plant-practice, where the water is returned again and again to the top of the mill, the

consumption of oil will probably be about ¼ lb. per ton of ore. This oil will cost, delivered, 8c. per pound.

Pine-tar oil is much cheaper. It gives good extraction, but the grade of concentrate is low. Cresylic acid, when used with pine-oils, increases the extraction about ¼ oz. silver per ton. This hardly pays for its use.

8. In the laboratory tests the grade of concentrate was low, averaging 200 oz. silver per ton. This concentrate could be raised to 1100 oz. by re-treating the concentrate by flotation.

9. Cyanide tests, run on tailing from the flotation tests, produced residues assaying less than 1 oz. silver per ton, with a cyanide consumption of less than 1 lb. per ton.

10. The dump-tailing cannot be easily treated by flotation. When the methods of flotation that are applicable to mine ore are applied to the dump-tailing, the results are *nil*. Furthermore, when the water that has been in contact with the dump-tailing is used for diluting mine-ore, the mine-ore cannot be treated advantageously by flotation. Experiments show that both these effects are due to the presence of soluble sulphates (chiefly those of magnesium and calcium) in the dump-tailing. The injurious effect of magnesium sulphate can be overcome largely by an excess of oil. No method of overcoming the injurious effects of calcium sulphate has yet been discovered in the tests.

When the dump-tailing is washed in fresh water half a dozen times, before being treated by flotation, the results of flotation are as satisfactory as is the case with mine-ore. However, a plant for washing the dump-tailing would be more expensive than the small tonnage of this material warrants, and the operation of such a plant would necessitate the waste of more water than is available. Some other method of rendering the dump-tailing susceptible to flotation may be devised; but the small tonnage does not warrant any extended investigation. The best thing to do, especially at the start, is to send the dump-tailing direct to the cyanide plant (after concentrating the ground sand on Wilfleys) as at present.

11. As a result of the laboratory experiment, it was decided

that full-sized tests should be conducted in the plant on run-of-mine ore.

Plant Tests.—For this purpose, there were set aside for the flotation circuit: one battery of five stamps, two Wilfley tables, one classifier, one tube-mill, one 24-ft. settler, and one pump for returning the water from the settling-tank to the head of the mill.

A flotation-cell of the pneumatic type was first tried. When treating 20-oz. heading this machine produced a 290-oz. concentrate and a 15.3-oz. tailing. This was far from satisfactory.

Another machine consisted of a series of mechanical-agitation chambers, alternating with a series of settling-chambers. From the start, this machine has given excellent results. In spite of many mechanical difficulties, and trouble with inexperienced operators, the tailing from the plant has averaged but little above 5 oz. silver per ton, and the concentrate has averaged above 600 oz., without re-concentration.

The chief weaknesses of mechanical agitation, as ascertained in this mill, are as follows:

1. The complex system of shafts and counter-shafts, with the corresponding drives, bearings, etc.

2. The difficulty of adjustment; any slight change in feed necessitating a change in the valves of each chamber.

3. The difficulty of the passages between chambers becoming clogged.

Submerged Agitation.—It has been attempted to evolve a flotation machine to overcome these weaknesses, and at the same time give results as good as the mechanical-agitation plant. A small machine (capacity 3 tons per day) has been constructed, and this, after many alterations, has yielded a 3.7-oz. tailing and a 680-oz. concentrate, when treating 10-oz. feed. This machine employs a somewhat novel principle of flotation—that of submerged agitation—the mixture of pulp, oil, and air being violently agitated in a partly closed chamber, under the hydrostatic pressure of several feet of pulp in the settling-chambers above.

In construction, this machine is simpler than the machine using mechanical agitation. It consists essentially of a V-shaped

box or trough, divided into compartments by a series of vertical partitions. At the bottom of each partition is an agitation-chamber. Agitation is supplied by a paddle-wheel in each chamber. All the paddle-wheels are mounted upon a single horizontal shafting, which passes the entire length of the trough, leaving the end partitions through stuffing-boxes. The pulp enters each agitation-chamber through an opening around the shafting, and leaves the agitation-chamber through an adjustable aperture, at a slight distance from the shafting. The agitator thus acts slightly as a centrifugal pump, overcoming the friction loss in the passage from one compartment to another, and keeping the height of the pulp the same in all the settling-chambers. The adjustment of the aperture is arranged to increase or decrease the centrifugal force. This adjustment occasions much less difficulty than is experienced in mechanical agitation, where the flow from one compartment to another is merely throttled.

Also, in the new plant there are no pipes to become clogged, the passage of pulp from one cell to another being along a rapidly revolving shafting, which keeps all material in suspension. The concentrate overflows from both edges of the trough, thus being removed more promptly than in a plant using mechanical agitation.

Further tests with the small machine are being made, and a larger machine (capacity 40 tons per day) is being constructed, for thoroughly testing the principles involved. The 40-ton machine will be constructed with the idea of using it for re-concentration of the concentrate, should a full-sized flotation plant be installed.

Simple Mechanical Agitation.—The machine has now been operating intermittently for a month. During that month it ran six days continuously, treating 25 tons of 29-oz. pulp and producing 6.4-oz. tailing and 600-oz. concentrate. During the first five days of the following month, careful tests were run to compare flotation results with those from current concentrating practice. The following tables give the summary of results from these tests.

Mill-Tests.—*Flotation v. Present Concentration Practice.*—Flotation plant takes 25 tons per day of mill-heading after being crushed to 20-mesh by stamps, concentrated on Wilfleys, and passed through a tube-mill.

METALLURGICAL RESULTS, PER TON OF ORIGINAL ORE, USING FLOTATION

	Tons.	Assay.		Contents.	
		Gold.	Silver.	Gold.	Silver.
Mill-heading	1.0000	0.125	39.81	0.125	29.81
Wilfley concentrate	0.0313	3.070	663.27	0.096	20.76
Wilfley tailing	0.9684	0.030	19.70	0.029	19.05
Flotation concentrate	0.0207	1.190	692.78	0.025	14.34
Flotation tailing	0.9477	0.004	4.98	0.004	4.71
Cyanide residue	....	0.001	1.00	0.001	0.95
Cyanide bullion	....	.....	.....	0.003	3.76

LIQUIDATIONS *

Wilfley and flotation concentrate, tons		0.52
Gold, 0.121 oz. at $20		$2.42
Silver, 35.10 oz., 95%=33.345 oz. at 50c		16.67
Copper, 3%−0.3=2.7%; 2.81 lb. at 8.2c		0.23
Lead, 11.8%−1.5=10.3%; 90% at 3c		0.29
		$19.61
Less haulage, freight, and treatment, at $19.67 per ton	$1.02	
Less taxes, commissions, etc., 7.44%	1.45	2.47
Bankable funds from concentrate per ton of ore		$17.14
Bullion from flotation tailing, per ton of ore, 5.56 oz. gross:		
Gold, 0.003 oz. at $20.67		$0.06
Silver, 3.76 oz. at 50c		1.88
		$1.94
Less haulage, treatment, 1.08c. per oz	$0.06	
Less express, duties, etc., 7.8%	0.15	0.21
Bankable funds from bullion per ton of ore		$1.73

* Throughout this article values are given in U. S. Currency.

PRODUCTS, PER TON OF ORIGINAL ORE

	Tons.	Assay.					
		Gold, oz.	Silver, oz.	Copper, %	Lead, %	Zinc, %	Insoluble, %
Wifley concentrate....	0.0313	3.07	663.27	2.75	12.00	12.7	24.5
Flotation concentrate.	0.0207	1.19	292.78	3.36	11.55	13.9	34.3
Average concentrate..	0.0520	2.327	675.00	3.00	11.80	13.2	28.4
Bullion.....	....	0.003	3.76	.....	.....	.....	.....

Present Practice.—During the five days the flotation test was being run, the rest of the mill received 160 tons per day of the same grade of mill-heading. This was treated on Wilfley and Deister tables and the tailing re-concentrated on Wilfleys and vanners.

METALLURGICAL RESULTS, PER TON OF ORIGINAL ORE

	Tons.	Assay.		Contents.	
		Gold.	Silver.	Gold.	Silver.
Mill-heading.....	1.00000	0.125	39.81	0.1250	39.81
Stamp-mill concentrate.....	0.03650	1.930	518.00	0.0706	18.94
Wilfley re-concentrate.....	0.00375	1.760	286.44	0.0066	1.08
Vanner re-concentrate.....	0.00060	0.780	370.92	0.0005	0.22
Tailing.....	0.95815	0.050	20.40	0.0473	19.57
Residue.....	0.95815	0.0048	3.12	0.0046	2.98
Bullion.....	.....	.....	.....	0.0427	16.59

Bullion, 24.88 oz. gross; gold, 0.0427 oz.; silver, 16.59 oz. per ton.

LIQUIDATION, PER TON OF ORIGINAL ORE

Concentrate, tons	0.04085
Gold, 0.0777 oz. at $20	$1.55
Silver, 20.24 oz.; 95% at 50c	9.61
Copper, 2.41%−0.3=2.11%; 1.73 lb. at 8.2c	0.14
Lead, 9.7%−1.5=8.2%; 90% at 3c	0.18
	$11.48

sustained in actual plant-practice, the saving in cyanide alone will amount to $3 \times 19c. = 57c.$ per ton of ore.

The present cost of precipitation and melting is 2.56c. per fine ounce.

In present practice 16.6 fine ounces is produced per ton of ore. When flotation tailing is treated, only 3.7 oz. is produced per ton of ore. This means an excess of 12.9 oz. produced in present practice: $129 \times 2.56c. = 33c.$ per ton of ore.

FINANCIAL STATEMENT

FLOTATION *v.* PRESENT PRACTICE, PER TON OF ORIGINAL ORE

	Present Practice.	Flotation.
Bankable funds; marketing concentrate	$9.82	$17.14
Bankable funds; marketing bullion	8.19	1.73
Increased cost of concentration	0.07	.....
Decreased cost of cyanide	.....	0.57
Decreased cost of melting and precipitation	.....	0.28
	$18.08	$19.72

Increased profit per ton from flotation, 200 tons per day at $1.64=$328 increased profit per day or $9840 increased profit per month.

The above is calculated on the basis of results from a single mill-test of five days duration. During this interval the heading to the mill and the residues were excessively high; indicating a greater advantage in favor of the flotation plant than is actually warranted.

The estimate of probable profit may be revised roughly by using the metallurgical results of the past two months for the basis of calculations. During two months the heading to the cyanide plant has averaged 17.8 oz. silver, and the residue has averaged 2.75 oz. per ton. The residue from cyanide-flotation tailing would assay 1 oz. per ton. This indicates an increased extraction of 1.75 oz. silver per ton of ore. 1.75 oz. at 41c. = 72c. increased profit per ton.

The indicated decrease in cyanide consumption (as determined solely in the laboratory) is 3 lb. per ton of ore. Reducing this to 2½ lb., to be on the safe side, the decreased cost of cyanide would be 2½ × 19c. = 47c. per ton of ore.

The decreased cost of precipitation and melting may be figured as follows: Cost of precipitation and melting, per fine ounce, has been 2.4c. The decreased production of bullion, due to flotation, would be 11 oz. per ton of ore. 11 oz. at 2.4c. = 26.4c. When fixed charges are considered, this should be reduced to 20c. per ton.

When the profit from marketing an increased amount of lead and copper is balanced against the increased loss occasioned by marketing the silver and gold as concentrate instead of bullion, there is a deficit of 17c. per ton of ore.

The matter may be summarized as follows:

	Per Ton.
Increased extraction	$0.72
Decreased cyanide consumption	0.47
Decreased cost of precipitation and melting	0.20
	$1.39
Increased cost of marketing	0.17
Profits per ton of ore	$1.22

The average tonnage of mine-ore for the past two months has been 5761 tons. Hence the indicated increase in monthly profit would be 5761 × $1.22 = $7028.42.

Installation of Flotation Plant.—Should a flotation plant be installed, operations in the stamp-mill will continue as at present; though it may be deemed advisable, after the flotation plant is running smoothly, to eliminate concentration in the stamp-mill, and depend upon the flotation plant for all concentration.

Re-concentration of current tailing on vanners and Wilfleys will be discontinued from the start.

The dump-tailing will be treated as at present, with the exception that this material will enter the plant only in the daytime. One tube-mill, one-classifier, one elevator, and the re-concentrating Wilfley tables will be kept separate from this circuit,

which will be in cyanide solution. All lime for the cyanide plant will enter this circuit. One of the 24-ft. tanks and one of the pumps must be reserved for the dump-tailing circuit.

All the tube-milling of current sand tailing will be done in mill-water, instead of cyanide solution.

The ground sand, together with the current slime, will be settled in two of the 24-ft. thickening-tanks, and will then enter the flotation plant. From the flotation plant, the tailing will flow to the two 33-ft. thickening-tanks. The thickened pulp from these tanks will be de-watered and washed in the vacuum-filter before entering the cyanide plant.

All lime for the mill-circuit will be added as an emulsion to the flotation-tailing launder, where it will be under direct control of the flotation-operator. The water in the 23-ft. thickening-tanks will contain about 0.4 lb. dissolved lime per ton. This is ample for good settling. The lime in the overflow will be reduced, by consumption, to about 0.1 lb. per ton. This is sufficient for fair settling in the cone-bottom tanks of the stamp-mill. By the time the pulp reaches the 24-ft. thickening-tanks the lime will be reduced to 0.03 lb. per ton. This low lime will be extremely detrimental to good settling in these tanks.

Installation Required.—The matter of supplying proper settling and de-watering facilities will be the most serious and most expensive part of the installation.

The two 24-ft. thickening-tanks, to be used in the flotation-circuit, must be triple-decked. It will also probably be found necessary to double-deck the 32-ft. steel thickening-tank. The work on settling-tanks will cost about $6000.

By increasing the settling capacity, the pulp will probably be settled to a sufficient thickness so that the vacuum-filter will be able to handle the combined sand-slime feed.

It may be found necessary, however, to add another unit to this plant. This will cost $2000.

The flotation plant will consist of two units (each of which will be able to treat the total tonnage of current tailing) and one smaller clean-up machine. The whole plant will cost about $3000. A filter-press for handling the concentrate will cost

$2000. Tanks, air-lifts, launders, and buildings will cost $2000. Thus the whole installation will cost $15,000, or $20,000 at the most. The addition of the flotation plant, for treating current tailing, will increase the profit about $7000 per month. Practically all ore from the mine may be treated by flotation.

FLOTATION AT THE CENTRAL MINE, BROKEN HILL[1]

By James Hebbard[2]

Early Attempts at Frothing.—While concentrating the galena in the lead ore produced from the Central mine, a valuable by-product was obtained in the form of slime assaying 18% lead, 20% zinc, and 16 oz. silver per ton. This came from an ore in which quartz and rhodonite were the chief gangue-minerals. In the course of ordinary operations, it had long been observed that a froth was formed containing high metallic contents, in silver and lead particularly, whenever conditions were favorable, as, for instance, where the rotation of trommels, or the splash of the elevators or raff-wheels, or the motion of the jig-plungers, produced a violent agitation of the mill-water containing slime. Early in 1901 a series of experiments was carried out for the purpose of reproducing and accentuating the conditions responsible for this valuable float-concentrate. Experiments and tests, extending over several months, were made on slimes of varying degrees of fineness. Among the appliances tried was a series of funnel-shaped vessels with the small ends downward, each fitted with an overflow-lip. The bottom end of the funnel or cone-shaped vessel was fitted with a tap or plug discharging the contents into the next vessel in the series, and so on. To each vessel was attached, near the bottom, a water-pipe, as well as a pipe carrying compressed air. The object of the water was to provide an upward current for the contents of the vessel, while the object of the compressed air was to produce agitation, and enhance the agitation effect of the up-current of water, in the

[1] From the *Mining and Scientific Press* of September 4, 1915. Abstract of paper appearing in the Proceedings of the Australasian Institute of Mining Engineers, November 10, 1913.

[2] Manager of the Central Mine, Broken Hill, New South Wales.

expectation of reproducing the conditions causing the "float" or metallic froth. Speaking generally, these experiments were on the lines of a spitzkasten, with a strong up-current to produce an agitation of the slime-water, assisted by jets of compressed air. It was thus early recognized that the bubbles of froth noticed in the wet-concentration operations were due to the aeration produced by violent agitation, resulting from mechanical implements moving rapidly in water. In these experiments a metallic

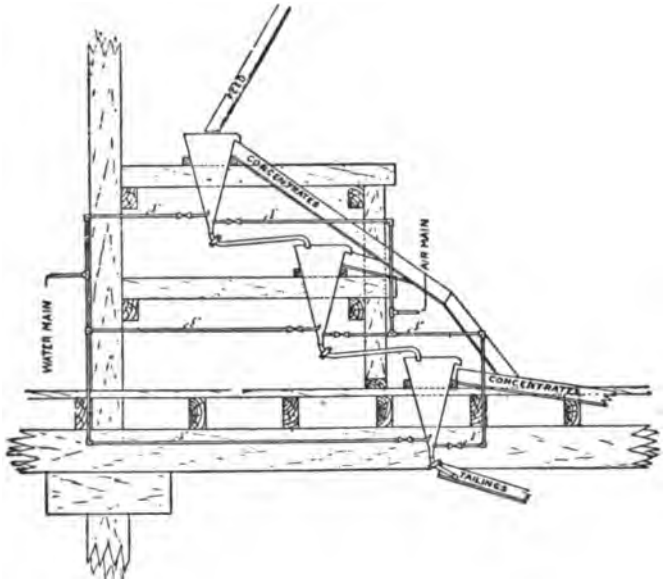


FIG. 1.—Apparatus for Experiments on Froth.

froth or scum could be produced and recovered assaying 26 oz. silver, 30% lead, and 22% zinc. The appliance employed is illustrated in Fig. 1.

[Up to that time the lead concentrate was the only marketable product from the ordinary water concentration. Besides calcite, the ore contained a good deal of rhodonite and garnet, each of which has a specific gravity close to that of blende. Thus water concentration could only yield a quartz tailing and a leady zinc-rhodonite-garnet middling.]

Preliminary Tests.—Early in 1903 an exhaustive series of laboratory tests was made on the lead by-product by flotation methods, using heated sulphuric acid and salt-cake solution. These tests yielded some slight measure of success on material specially prepared, that is, on grainy material from which both the coarse and fine had been eliminated, leaving it evenly sized. Certain classes of the material produced by our mills contained such a large proportion of carbonates—such as carbonates of manganese, lime, and lead—that no flotation could be secured except by a prohibitive consumption of acid. These tests were carefully made, but the best work done in the laboratory was not equal to that being secured on a commercial scale in the existing magnetic plant. The tests on these flotation methods were conducted in pans or vessels worked on the principles of spitzkasten, following the lines of Potter and Delprat. The first apparatus was constructed so that the liquors could be raised in temperature by the application of direct heat underneath the pan; but in the later types the temperature of the liquor in the pan or spitz-box was maintained by the injection of live steam into the storage-tank. In none of these tests was agitation employed, the material to be treated being fed practically dry on the surface of the liquor in a regular stream, and the heated liquor added through a pipe discharging near the bottom of the vessel, and given an upward inclination in order to produce an up-current in the box itself and a gentle overflow at the lip. A still surface was imperative in this operation, and it was equally evident that the operation depended largely for its success on surface-tension of the liquor, after the gas evolved by the action of the acid on the mineral carbonates had raised the particles. This surface-tension was increased by the density attained in the one case by the salts formed from the mineral and gangue through the action of the sulphuric acid, and in the other by the addition of salt-cake. In all these experiments the liquor was returned by the ordinary type of air-lift, using compressed air at about 70-lb. pressure. These experiments definitely demonstrated:

1. That there was a limit to the size of the particle that could be buoyed up.

2. That any material below a certain size, no matter what its character—whether gangue or mineral—floated, owing to the density of the solution.

3. That if the finer particles of gangue were not eliminated before treatment they would be floated with the mineral, and lower its value in metals to such an extent as to make it unmarketable.

Slime, whether existing as a by-product of the ordinary wet-mill concentration or subsequently produced in preparing tailing for treatment, bulked so largely among the total material available for re-treatment that any process that failed in this direction was too limited in its scope to be of much value to the Central mine.

As far as any process up to date was concerned, slime had to be regarded as of no value except in so far as it was available for smelting. The Broken Hill Proprietary Co. had used a considerable quantity in this way, and had discovered that roasting or sintering the slime in open heaps after briquetting gave a fair product valuable for smelting, a good deal of the sulphur and a fair proportion of the zinc having been driven off. The Sulphide Corporation also sought to make its slime available by this means, but it was proved that the losses of metal were too great to justify this method of rendering the slime amenable to direct smelting.

Cattermole or Granulation Process.—The foregoing experiments were abandoned on account of information received from London. C. F. Courtney, who was in England during the year 1902, advised that a discovery of considerable importance had been made; that laboratory trials gave every indication of success on a large scale; and that the process was so comprehensive as to include the finest slime and varying coarser sizes of particles up to ½ mm. diam. This was subsequently known as the Cattermole or granulation process, and consisted in the agitation of a mixture of pulp, oil, and water, containing a suitable acid, or an alkali with soap or other emulsifying agent, so as to agglomerate the oil-coated particles into granules. The oil was thus employed in a state of emulsion in water in the presence of an emulsifying agent, such as soap. After agitation the mixture

was passed into an up-current separator or classifier to remove the lighter non-oil-coated particles from the agglomerated masses of oil-coated particles. The lighter sand having been removed, the pulp passed to a second series of agitators to increase the size of the granules, and thence to a second classifier for the removal of the heavy sand. From the bottom of this second classifier some granulated concentrate was recovered, but the heavy sand from the overflow also carried over, with the up-current, a large amount of granulated mineral. This mixture of granulated mineral and heavy sand passed then to a third series of agitators, and thence to a shaking-table, where the granulated mineral, rendered more buoyant by directing jets of compressed air onto the surface of the moist pulp, was buoyed to the surface of the water and floated off the bottom of the table, while the gangue sank and was delivered over the end of the table.

In order to give this process a thorough trial, a model plant was sent from England and erected on the mine early in 1904. G. A. Chapman was specially appointed to conduct experiments with this plant, and started a long series of tests early in June of the same year. It was quickly demonstrated that the process was capable of making high recoveries of all the three metals from the very finest slime, whether taken from the current work of the mill or from old accumulations, and also that old tailing or new crude ore was amenable to treatment when crushed to a given fineness. The largest size of particle that could be recovered was ascertained to be about ½ mm., thus confirming the London work; but it was found that results improved with a decrease in size to impalpability.

In the early tests by Mr. Chapman, emulsions of the heavy oil of petroleum were used, but the cost was excessive, and it was found impossible to treat slime successfully. Emulsions of fatty acids, and also soft soap, were then tried, but proved prohibitive as to cost, except in the case of oleic acid. Oleic-acid emulsion was found to act rapidly and effectively on crude ore as well as on all lead by-products, including slime.

Mr. Chapman's work on oils and the results obtained by him with the model plant using the granulation process were satis-

factory, but it was thought wise to have these confirmed by an independent chemist, and therefore J. C. Moulden, the company's chief metallurgist at Cockle Creek, was called in, repeated the experiments, and amply confirmed Mr. Chapman's work. Later it was found possible also to reduce the quantity of oleic acid, as was proved by the following tests in December, 1904:

Material used was crushed tailing mixed with slime.

Test No. 1. 3.5% oleic acid on mineral and 0.75% sulphuric-acid circuit.

The cost of emulsion in this case was 10s. per ton of ore, but the results were excellent, the concentrate being recovered as partly granulated and partly float or froth.

In test No. 2, only 0.75% of oleic acid with the same (0.75%) sulphuric-acid circuit, in which case the cost of emulsion amounted to 2s. 3d. per ton of ore, the results being excellent, with all float concentrate, no granular material being formed. This test took considerably longer agitation.

Erection of Large Plant.—Mr. Chapman's tests, and their confirmation by Mr. Moulden, established the fact that a process was obtained that would, with suitable arrangements for crushing, efficiently handle the whole of the by-products of the wet mill, including slime. It was accordingly decided to erect a plant on the lines of the model, with slight modifications as dictated by experience, capable of treating 100 tons per day, operating on a commercial scale.

It was clear, from experiments and observations, that the time of agitation was a factor in the aeration and oiling of the mineral particles. Therefore, reckoning from the size and capacity of the mixers in the model plant, a mixer was built of the following dimensions: 5 ft. deep and 3 ft. diam., with a wooden stirrer 2 ft. 6 in. diam. at bottom placed vertically and made to revolve at the rate of 350 r. p. m.

Experiments with this one mixer unit indicated that, to make the treatment continuous for the stipulated 100 tons per day, it would be necessary to have for the first unit a series of six mixers in order to allow of the proper cleaning of the particles and the thorough aeration of the whole mixture before the discharge of

the material under treatment from the last of the series. The mixer was of the core-stirrer type.

Accordingly, the plant was designed on these lines, and consisted of :

1. Grinding apparatus.
2. Vat for emulsifying various oils.
3. Set of six mixers in series.
4. Upcasts for separating sand and float.
5. Second set of mixers for further aeration.
6. Upcasts for further separation of sand and float.
7. Third set of mixers for re-aeration.
8. Wilfley tables for the separation of coarse sand from granulated sulphide.

Early in 1905 the construction of this plant was commenced; it was completed at a cost of £11,000, and started work in July, 1905. The method of treatment adopted was on the lines of the tests made in the experimental model plant, and may be briefly described. See Fig. 2.

The ore, reduced to a suitable fineness, was elevated to a hopper at the top of the building and fed into No. 1 mixer, where it was agitated with the solution, the emulsion (previously prepared on the bottom floor) being added at the same time, together with further sulphuric acid, if required. The feed of ground material and the addition of the circuit-liquor and reagents was maintained constantly and regularly. After passing through the first set of six mixers a pulp consisting of ground ore, acidulated water, and emulsion was passed to a hydraulic-sizing appliance known as an upcast, where the slime-gangue was removed by overflowing. The balance of the mixture was passed into the second set of mixers, beginning with No. 7, where more emulsion and sulphuric acid were added if necessary. The agitation and aeration were maintained and the pulp discharged from No. 9 into another upcast, where further slime-gangue was removed by overflow. The balance of the material was then passed to No. 10 mixer, and thence through No. 12 to the Wilfley tables. The separation on the tables was effected thus: Such concentrate as had been frothed by the aeration and agitation passed

off the table immediately opposite the point of feeding. The granulated or " air-bally " material remained in close contact with the table, along with the sand, but floated immediately under the influence of puffs of air (supplied through a pipe laid lengthwise and close to the table), and then floated off with the froth concentrate. The sand was delivered toward and at the end of the table, thus exactly reversing the relative positions of

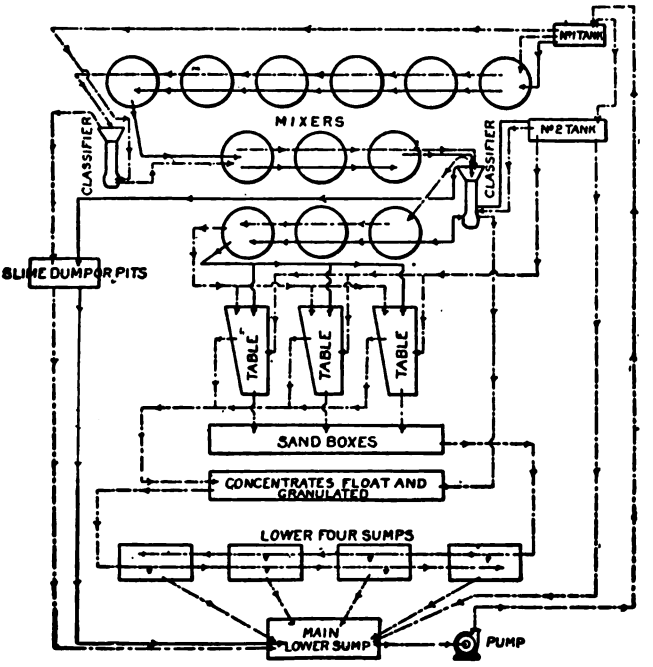


FIG. 2.—The Experimental Model Plant.

concentrate and tailing as ordinarily obtained if working by gravity concentration. The slime and sand were collected in one receptacle and the float and granulated concentrate in another, the surplus liquors in each case flowing to a common sump for re-use.

From the first day of operation the ease with which the float concentrate could be recovered was very striking; but the separation of the granulated concentrate from the coarse sand by ta-

bling on a large scale was found to be a very delicate and difficult operation, and it was at once evident that "spitz" separation would relieve the tables. The upcasts were also continually choking and proving a source of trouble, besides sending over large quantities of slime with the concentrate, thus reducing the grade of the product and lessening its market-value.

It was therefore decided, when the plant had been running for a few days only, to construct a small rectangular spitz-box for trial. This was introduced early in August, 1905, the feed to the spitz-box being prepared pulp discharged from No. 7 mixer.

It was found also, as soon as the plant started regular treatment, that the agitation was excessive, and mixers 10, 11, and 12 were cut out.

Cone-agitators made of phosphor bronze were tried, then centrifugal stirrers, but the scour both on the stirrer and the sides of the mixer, due to the impact of the sand, was so great that these had to be abandoned, although the agitation and aeration had been considerably increased.

The spitz-box in the slime-overflow circuit gave excellent results, and toward the end of August it was possible to obtain the requisite agitation by using the first six mixers only. A fresh spitz-box was placed in the position formerly occupied by vats 7 and 8, with arrangements for all tailing-flows, both slimes and sands, to deliver to No. 1 hutch of a special spitz on the floor beneath. The object of this spitz (3-compartment) was (1) to allow a settlement of the granulated material in the first compartment; (2) to effect a settlement of middling for re-treatment on tables in the second; (3) to provide for the deposition of clean sand and slime in the third, with an unrestricted overflow for the float material. Sprays on the surface of the liquor, and upcasting jets of water, were provided to assist the operation. Various simplified forms were later adopted as the process merged from partial to complete flotation, as illustrated in the experimental spitz-box for the granulation plant (Fig. 3).

At first the sand was ejected by sluicing out to a dam; but this being wasteful of circuit-liquor, and therefore also acid, it

was decided to construct sand-boxes, through which, in turn, the suspended sand could be deposited—the liquor overflowing from these sand-boxes to be run to the pump-sump and thence re-circulated through the plant. By this means a closed circuit would be secured, and liquor-losses minimized. It was not until November that these sand-boxes were actually in use. Meantime, it was noted, particularly in slime-tests, that the operation was appreciably assisted by raising the temperature of the liquor. Steam jets were, therefore, introduced into the mixers in the plant early in September, 1905.

Before advancing further with the evolution of the process as developed in the first large plant, it is perhaps advisable to

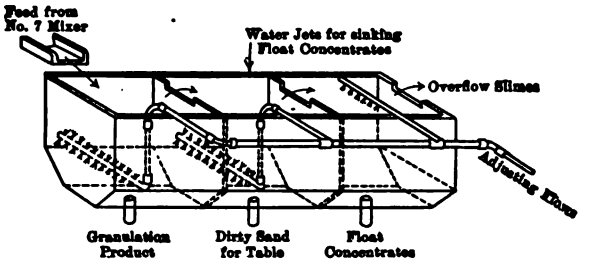


FIG. 3.—Experimental Spitz-Box.

refer here to certain experiments that mark a most important era in the history of the process.

Discovery of the Frothing Process.—We now come to a stage when a remarkable development in the operation was discovered (strangely enough, at the same time both here and in the Patent Co.'s [1] laboratory in London), which had for its main principle the reversal of all previous operations, and consisted in the complete flotation of each particle of mineral independently in place of granulating the mineral particles and causing them to sink, thus not only revolutionizing the process, but greatly simplifying and cheapening it. The developments noted were mainly along the line of decreased consumption of oleic acid or oil, for example, from 3% oleic on ore, resulting in very little float, down to 1%, giving practically a complete float.

[1] [Minerals Separation Ltd.—EDITOR.]

The following data from a report furnished by A. H. Higgins (March 16, 1905), indicate in more detail the nature of the experiments and the effect on the separation produced by varying the percentage of oleic acid.

DETAILS OF EXPERIMENTS

Acid, %	Oleic, c.c.	Percentage of Oleic on Ore.	Time for Aeration, Min.	Temperature, C.	Remarks.
1.1	15.0	3.0	4	30.5°	Very little float
1.1	7.5	1.5	4½	31.0°	Rather more float
1.1	5.2	1.04	6	31.0°	Still more float
1.1	3.1	0.62	6	32.0°	Still more float
1.1	1.66	0.32	7	31.0°	Float vastly increased
1.1	0.5	0.10	8	31.0°	Float vastly increased

In every case the oleic acid has been measured in cubic centimetres and the percentages calculated as though they weighed grains; but, as the specific gravity of oleic is less than that of water (taken as 1), all percentages will be lower than those actually given.

These experiments obviously proved that the reduction in the percentage of oleic acid materially altered the type or character of the oiling of the mineral particles—the higher percentage producing granules, which were precipitated, while the lower percentages produced a mineral froth. As the quantity of oleic acid decreased, the time required for oiling the mineral particles and aerating them was found to increase, and more froth formed. These tests, followed by many others, led to Messrs. Sulman, Picard, and Ballot's British patent of April 12, 1905, under which "finely powdered ore, suspended in acidified water, is mixed with a small proportion of an oily substance such as oleic acid, amounting to a fraction of 1% on the ore, and agitated until the oil-coated minerals form into a froth, which can be separated from the gangue by flotation. Heat may be applied to facilitate oiling and either shaking tables or spitz-boxes may be used to separate the frothy mineral from the sands and the gangue slime."

To return now to the record of operations at the large plant, some successful tests were carried out in September, 1905, on dump-slime, by using this flotation method. Agitation was completed in six mixers (using cones) in 0.6 to 1% sulphuric acid at a temperature of 80–90° F. The quantity of oleic acid used in these tests was from 0.15 to 0.2% on the actual dry weight of slime treated. From the sixth mixer the pulp passed " with a good splash " to the first spitz, and the residues from this " with a good splash " to No. 2 spitz, and the tailing from this latter spitz-box was run into dams. These and other experiments emphasized the importance of dropping the pulp vertically into the spitz to assist aeration and subsequent flotation, and of heating the liquor to enhance the oiling of mineral particles.

The three-compartment spitz-box with upcast water-flows gave place, in turn, to a two-compartment spitz-box without upcast flow, and this, in turn, was replaced by a single-compartment spitz, the latter being provided with a rigid flat board on which the feed was splashed to assist aeration. Conical spitz-boxes were tried, but not generally adopted.

From Granulation to Flotation.—The plant had now been running for a couple of months on tailings and slimes from various sources, and during this time the frothing method was generally ousting the granulation process, until, finally, the superiority of the spitz-box and froth method was clearly demonstrated. The Wilfley tables of the original plant were then dismantled to make room for the sand-boxes already mentioned, and the granulation gave way to flotation with simple spitz-boxes early in October, after treatment of approximately 1700 tons of crude ore, tailing, and slime.

This method of working, thus briefly outlined, quickly established itself as capable of dealing with the company's ores and by-products, and Mr. Chapman's patent of September, 1906, was taken out to protect the various discoveries made by supplementing Sulman, Picard, and Ballot's patent (No. 5032, 1905). Under Mr. Chapman's patent:

1. The ore, suitably crushed, is agitated with acidified water in the first mixer and heated.

2. Oleic acid is subsequently added in the second vessel.

3. The pulp is maintained at the desired temperature in the third and following mixers, with violent agitation in each mixer to insure complete and thorough aeration. A sequence of operations is thus arranged by which the solution, after the second agitator, is practically or entirely neutralized, so that the liquor in circuit as a whole is neutral, except at the outset, when the ore is introduced.

The adoption of this flotation process with its neutral liquor allowed the use of iron where formerly, under the granulation method, with acid liquor, only wood or special metal could be used. For instance, the original wooden-cone mixers, which had been replaced by centrifugal stirrers of copper or beaters of regulus metal, were now replaced by four-armed stirrers of cast-iron.

A great difficulty lay in the grinding. The experiments had proved that the best work could be obtained on material that would pass through 40-mesh, and that practically the finer the material the better the recovery. The whole experience in the fine grinding had been with ball-mills in our magnetic plant, and accordingly a No. 8 Krupp dry ball-mill was attached to this plant as part of the equipment. The dry mill proved unsuitable, and, with considerable difficulty, it was converted to a wet mill. Even then its capacity, allowing for numerous break-downs partly due to forcing its capacity, was too limited, and two No. 5 Krupp wet ball-mills were installed to assist. Meantime, experiments proved conclusively that grinding-pans were superior in character of work, cost of maintenance, and power consumed, to the ball-mills for re-grinding tailing, whereupon we installed a grinding-plant which was gradually increased until the ball-mills were thrown out of use entirely. The character of the work was much improved, and it was then evident how much the progress of the process to a satisfactory stage of efficiency had been retarded by lack of efficient grinding appliances.

Extension of Plant.—The operations of the first plant were commercially and technically successful, and an extension was completed, with all its appurtenances, including grinding-pans for the reduction of the material to the requisite degree of com-

minution, conveyor-belts for the disposal of the residues, together with bins for concentrates and tanks for storage of liquor, toward the end of 1906, at a cost of £25,000, the sum of £11,000 having been already spent on the initial experimental plant. The total quantity of material treated by this flotation plant was 135,808 tons, which yielded 45,147 tons of high-grade zinc concentrate. The plant continued in successful operation until the completion of the wet-mill zinc section, which was capable of supplying the quantity of zinc concentrate under contract. During the time this plant was in operation numerous tests were made with a view to increasing the aeration, which was recognized as the chief

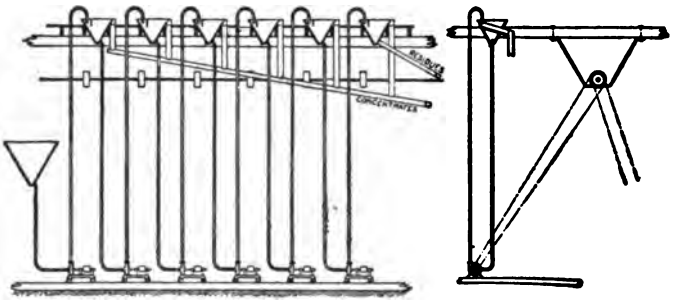


FIG. 4.—A Nest of Centrifugal Pumps.

factor in flotation, and at the same time lessening the mechanical energy absorbed in aerating. Among these may be mentioned the nest of centrifugal pumps, as illustrated in Fig. 4. The pumps were worked in series, each one drawing a tailing from the preceding spitz and discharging into the next succeeding spitz. The aeration and flotation were produced satisfactorily, but it was soon found that the scour in the pumps, caused by the gritty nature of the material being pumped, was so great that the heavy maintenance would counteract the other advantages. Another expedient was to lift the whole of the tailing discharged from the first spitz by means of an air-lift. This also resulted in increased aeration, but it was found that the volume of liquor would have to be increased to an impracticable quantity to give the necessary velocity to carry the particles of ore, etc., up the rising leg

of the pipe and prevent settling. An elevator was subsequently installed in its place to command the third spitz of the series. Further expedients were the insertion of a jet of air into a centrifugal pump used for raising liquors and material for re-treatment, the introduction of a jet of compressed air into the mixer-boxes, and also the insertion of pipes in the mixer-boxes in such a position that air would be drawn into the bottom of the mixer by the rotation of the blades. As a result of all these expedients, the conclusion was formed that the air, to be of value, must be finely comminuted, but that any addition was of value that would decrease the energy required to secure aeration by means of mechanical agitation.

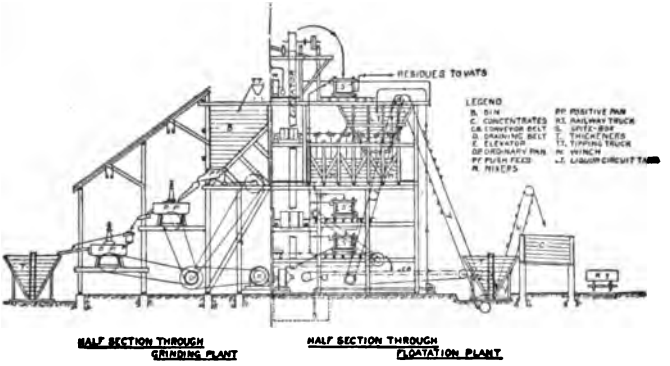


FIG. 5.—The Plant at the Central Mine.

Minerals Separation Plant.—The Minerals Separation company, owners of the froth patents, purchased the tailing-dumps on the Central mine, and, by arrangement, a plant was designed and erected by the Sulphide Corporation for their treatment. The plant is shown in cross-section in Fig. 5, and was designed on previous experience for the treatment of 2000 tons per week. It was finished at a cost of £26,000 complete. The efficiency of the grinding-pans proved so great with the new design of positive pan that the plant was able easily to handle 5000 tons per week. This plant was responsible for the treatment of 709,999 tons of tailing, etc., and the production of 242,462 tons of concentrate up to the time it was shut-down in June, 1911, on the exhaustion of the dumps.

In connection with the Minerals Separation plant, it is important to note that the fact of the circuit being no longer acid, but neutral, has been taken advantage of, inasmuch as there is only one circuit through iron grinding-pans, agitators, and spitz-boxes. The original granulation plant, being designed for an acid circuit, was equipped originally with wood throughout where liquor circulated, and with dry-crushing ball-mills for the same reason. Later, wet crushing was adopted, but with a fresh-water circuit, kept carefully separate from the acid circuit in which the actual separation took place. The successful development of the flotation process, however, has enabled both crushing and separation to be conducted in one and the same circuit, and has thus greatly simplified operations.

The liquor that was circulated through the Minerals Separation plant was approximately 25,000 gal. per hour. During the course of operation, therefore, over 600,000,000 gal.—equal to nearly 3,000,000 tons—has passed through the 12 iron grinding-pans of this plant without detrimental effect. No stronger evidence could be produced as to the freedom of the circuit-liquor from acidity. The maintenance charges on these iron pans are no heavier than corresponding charges on exactly similar grinding-pans in the lead-mill crusher-section, where fresh water only is used.

Following exhaustive experiments in the laboratory, various media have from time to time been used for long periods on the commercial scale, both in substitution for and in combination with oleic acid. Chief among such media are amyl alcohol, resin-oil, camphor-oil, pine-oil, and eucalyptus, with all of which ingredients good work has been obtained. Thus Nature, in close proximity to the vast bodies of complex ore, has provided the means for the concentration of such ores, for the essential oil of the Australian eucalyptus is one of the best-known media available for the successful exploitation of refractory Australian ores. It is of interest to note here that this application of an Australian product to the treatment of complex ores is the outcome of research at the Central mine by an Australian metallurgist, Henry Lavers; and it was also in the milling-plant on the Central mine that

Results Obtained.—For comparison with the work of the old mill, the following summary of results achieved by the existing plant will be of interest. This table summarizes work done on a commercial scale in the Central mill over a period of twelve months, ending December 28, 1912, and demonstrates conclusively the vast improvement in concentration practice made possible by the adoption of the flotation process.

SUMMARY

	Prop.,	Assay Value.			Recoveries.		
	%	Ag, oz.	Pb, %	Zn, %	Ag, %	Pb, %	Zn, %
Lead concentrate ex lead section....	16.0	33.1	67.0	6.7	44.7	72.4	6.1
Lead concentrate ex de-lead plant..	1.4	50.9	62.5	12.5	5.9	5.8	1.0
Total lead concentrate.....	17.4	34.5	66.7	7.1	50.6	78.2	7.1
Zinc concentrate.....	32.7	16.1	8.1	46.4	42.1	15.9	84.7
Total concentrates.....	50.1	...	...	...	92.7	94.1	91.8

Modifications of the wet mill are now in hand for the improvement of the grinding, but it is felt that, as the proportion of lower-level ore increases, the grinding appliances will have to be increased in order to allow for the finer crystallization of the minerals in the ore as further depth is attained. The author is of the opinion that the figures quoted clearly show that if the ideal grinding is obtained the already high recoveries of metals will be further augmented.

It is unique in the history of concentration that so far-reaching and extensive a development should have reached its present state of perfection in so short a space of time, and more wonderful still that it should prove applicable in an equally masterly manner to so many other classes of ore. There can be little doubt left in the minds of those who have seen this new system of concentration that it must of necessity spread to all parts of the world.

CYANIDE TREATMENT OF FLOTATION CONCENTRATE[1]

By Charles Butters and J. E Clennell

When Charles Butters began to take up the work of flotation in our Oakland laboratory, one of the first points brought to our attention was the treatment of the concentrate produced by flotation; J. E. Clennell was accordingly instructed to undertake the researches detailed in the present paper.

The whole value of the process hinges on two points, namely, the grade of tailing produced and the net realization of the value contained in the concentrate, these two considerations being of equal importance. This last point is complicated by questions of geographical situation, for if the concentrate cannot be treated locally the cost of realization may be so heavy that flotation would be entirely precluded.

The results obtained in our laboratory by the combination of flotation and cyanide have been so remarkable that a serious study of the disposal of concentrates has been forced upon us.

The difficulties attending the treatment of concentrate by cyanide are well known. The process of concentration collects in a small bulk not only the valuable constituents of the ore but also those substances that act as cyanicides, or which are readily converted by oxidation or otherwise into cyanicides, so that their influence, per ton of material treated, is greater than would be the case with the unconcentrated ore. Heavy minerals such as the sulphides of iron, copper, lead, arsenic, antimony, zinc, and double sulphides such as mispickel, proustite, pyrargyrite, and bornite, naturally tend to accumulate in the concentrate. If some interval elapses between the formation of this concentrate and its treatment, oxidation may take place, with formation of sulphates, arsenates, and antimonates, which are still more detri-

[1] From the *Mining and Scientific Press* of November 20, 1915.

mental to cyanide treatment than the original minerals. These difficulties have been wholly or partly overcome by the adoption of modifications in the treatment, such as preliminary water, acid, or alkali washing, roasting, fine grinding, the use of special solvents, such as bromo-cyanide, and prolonged contact of the material with cyanide, extending in some cases to over a month.

In the case of concentrate produced by flotation, the minerals composing the product are substantially the same as those obtained by gravity-concentration, consisting of the sulphides and double sulphides of the heavy metals, and it is to be expected that the same difficulties will be encountered in their treatment. But as the concentrate also contains a considerable part of the oil, tar, or other flotation-agent, the presence of this foreign matter must be taken into account. In some cases, this circumstance introduces an additional difficulty. A part of this organic matter is soluble in the cyanide or alkali used in the process, and the solution so formed may be capable of absorbing oxygen. The effect produced by carbonaceous matter in precipitating gold and silver previously dissolved by cyanide is well known and has been a source of much trouble in many localities. Some of the constituents of this matter are not easily eliminated and appear to resist oxidation even at a high temperature; roasting under ordinary conditions does not completely remove the carbon; it is probable that a portion derived from tar remains in the graphitic form, capable of acting as a precipitant for gold or silver.

The experiments detailed below were made on concentrates produced from typical gold and silver ores by a modified type of the Minerals Separation flotation machine. Most of the tests were made in neutral or alkaline media. The frothing-agents employed were those in general use, consisting of tar, creosote, carbolic acid, pine-oil, and fuel-oil. It is not proposed to discuss these in detail in the present paper; it will be sufficient to state that the concentrate was collected and drained on a vacuum-filter and in some cases dried at a moderate temperature before treatment.

As an example of an ore in which the value consists essentially of gold we may take the product of the San Sebastian mine, in

Salvador, operated by the Butters Salvador Mines, Ltd. For preliminary work a composite sample was made from 21 lots taken from different parts of the mine, and concentrate produced by treating the finely crushed ore in a 10-lb. flotation machine. The sample taken for this test assayed originally 1.54 oz. gold and 0.28 oz. silver. The concentrate obtained by flotation assayed 4.92 oz. gold and 1.14 oz. silver. As this constituted 25% of the weight of ore taken, the gold recovered in the concentrate amounted to 79.9% of the total. An analysis of the concentrate showed:

	%		%
Insoluble	44.3	Iron	24.3
Sulphur	26.2	Copper	0.8

together with small quantities of molybdenum, tellurium, and other elements. The tailing carried 0.04 oz. gold per ton.

The first tests were made with the object of determining whether this material could be treated advantageously raw by agitation with cyanide. In addition to direct cyanide treatment various modifications were tried, as shown in Table I, including addition of lead acetate, preliminary alkali treatment, desulphurizing with alkali and aluminum, and bromo-cyanide. The last procedure showed a marked improvement over every other method of raw treatment, but still failed to yield a satisfactory extraction. The extraction was increased by increasing cyanide strength, but with strong solution the consumption of cyanide became prohibitive, and alkaline sulphides were formed. This effect can be prevented and cyanide consumption much reduced by addition of lead acetate, some improvement in extraction being obtained. Preliminary alkali treatment with or without aluminum showed no benefit whatever. The fact that bromo-cyanide has a marked effect on the extraction suggests that a portion of the gold may be present as a telluride. This conclusion is supported by experiments made by direct treatment of the original ore, without concentration; these tests showed that a certain proportion of the gold is unamenable to cyanide even after very fine grinding and prolonged contact. (See Table XI.)

TABLE I

Summary of Results in Treatment of Raw Concentrate

	Gold, oz.	Silver, oz.
Head assay for all tests	4.92	1.14

Dilution in all tests, 3 : 1.

Test No.	Method.	Time, Days.	Cyanide Strength, KCN, %	Chemicals Consumed per Ton.			Residue Assay.		Extraction.	
				Cyanide, lb.	Lead Acetate, lb.	BrCN, lb.	Gold, oz.	Silver, oz.	Gold, %	Silver, %
1	Direct cyanide	3	0.25	32.7	..	..	4.38	1.06	11.0	7.0
2	" "	3	0.5	39.1	..	..	3.88	0.88	21.1	22.8
3	" "	3	1.0	52.3	..	..	3.46	0.70	29.7	38.6
4	With lead acetate	3	0.25	19.5	10	..	3.02	0.74	38.4	35.1
5	Preliminary NaOH	5	0.25	35.9	..	..	3.76	1.00	23.6	12.3
6	Preliminary NaOH+Al	5	0.25	35.9	..	..	3.68	1.00	25.2	12.3
7	Bromo-cyanide	8	0.25	41.1	..	8.3	1.20	0.68	75.6	40.4
8	Similar to No. 7, but without bromo-cyanide	8	0.25	35.5	..	..	3.50	0.86	28.9	33.3

As these results did not appear encouraging for any system of raw treatment, attention was next turned to roasting. It was soon found that roasting within certain limits of temperature converted a considerable part of the copper into sulphate, which could be leached with water, together with some sulphate of iron, leaving the residue in a favorable condition for cyanide treatment. Preliminary acid-wash of the roasted material was also tried; this would have the advantage of dissolving a further quantity of copper that might have become converted into oxide in the roasting, but the results show that the benefit obtained would not warrant the additional cost. Another test was made in which the concentrate was cyanided raw before roasting and acid-washing, and re-cyanided after washing; this also showed no advantage either in extraction or cyanide consumption over direct roasting, water-wash, and cyanide. In all cases the roasted material was agitated with cyanide, using a dilution of 3 : 1. The results obtained by these three methods are shown in the following table. (No. II.)

In Test No. 2 the acid-washing was made with 1% H_2SO_4, using approximately 5 tons of wash per ton of concentrate treated. Before agitation with cyanide, the pulp was re-ground in a model tube-mill with glass marbles.

In Test No. 3 the preliminary raw treatment was made with 0.1% KCN using a dilution of 2 : 1, for two days; the extraction of gold was 12%. Acid treatment was made with 1% H_2SO_4, dilution 1 : 1, agitated 18 hours, and then leached with water before cyaniding. Roasted and washed concentrate was agitated with cyanide for 4 days.

Test No. 1 on Table II indicates that the flotation concentrate from the San Sebastian ore may be successfully treated by a simple process of roasting, water-washing, and cyaniding. This conclusion was confirmed by numerous experiments on a large scale in which the material was roasted in a hand-reverberatory furnace, and the roasted product treated by agitation in tanks with mechanical stirrers, adding water, settling, and decanting until the bulk of the copper and iron salts was removed, finally collecting the material on a vacuum-filter and washing on the

TABLE II

COMPARATIVE RESULTS OF CYANIDING AFTER ROAST WITH VARIOUS PRELIMINARY TREATMENTS

Test No.	Time under Cyanide, Days.	Strength Used KCN, %	Cyanide Consumed per Ton of Raw Concentrate, lb.	Weight of 1 Ton Raw Concentrate after Treatment Ton.	Assay of Raw Concentrate.		Assay of Roasted and Washed Concentrate.		Residue of Treated Material.		Calculated Residue on Raw Concentrate.		Recovery * Based on Raw Concentrate.	
					Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, %	Silver, %
1	3	0.25	4.20	0.792	4.92	1.14	6.20	1.44	0.15	1.37	0.12	1.09	97.5	4.9
2	3	0.25	6.49	0.790	4.92	1.14	6.28	1.36	0.125	1.20	0.10	0.95	98.8	11.1
3	6	0.10	8.93	0.773	4.92	1.14	5.44	1.44	2.00	1.28	1.55	0.99	64.9	10.9

* In calculating "recovery," allowance is made for losses of gold and silver in roasting.

Test No. 1. Oxidizing roast, water-wash, and cyanide.

Test No. 2. Oxidizing roast, acid-wash, and cyanide.

Test No. 3. Cyaniding raw, roasting, acid-wash, and re-cyaniding.

filter to remove the last traces of soluble salts. The washed concentrate was then re-pulped with lime and cyanide solution in an agitation-tank, and treatment continued in the ordinary way. The results of bottle-tests were fully confirmed.

Attempts to treat the material by percolation were not successful. Owing to the fine grinding of the ore previous to flotation, the roasted material showed a tendency to slime; percolation took place slowly and irregularly, through channels formed in the mass, so that the extraction by this means was always imperfect.

In the tests made in the large muffle the oxidation was somewhat more effective, but a rather longer time was required to reach the temperature at which roasting began. Temperature was approximately determined by Seger cones.

On examining the details of Table III, it will be apparent that the most favorable results were obtained when roasting was carried out at a low temperature; under these conditions a maximum amount of copper was extracted by water-washing, and the highest extraction of gold obtained with a minimum cyanide consumption.

In this ore the silver is negligible, but it is significant that the silver extraction on the roasted material is poor in all cases. This condition will be noted in most cases where attempts have been made to treat silver ores by cyanide after an oxidizing roast.

With these results as a guide, tests were made on a larger scale on the same material, roasted by hand in an oil-fired reverberatory furnace. A charge of about 400 lb. was dried slowly in a sample-drier, and charged into the furnace; the temperature was gradually raised till it approximated that obtained in the muffle-roasts, probably about 550° C. After 3½ hours, the flame was turned off and the charge allowed to cool in the furnace overnight. The concentrate, roasted in this way, showed little or no tendency to sinter or form lumps, but in subsequent tests when the material was charged without previous drying, portions of the concentrate agglomerated into comparatively hard lumps, which contained a core of unroasted material, and which it was necessary to sift out and re-roast after grinding. Possibly in practice it would be advisable to pass the material, after

TABLE III—(*Continued*)

Test No.	Head Assays.						Residue Assays after Cyanide.			
	Roasted Concentrate.		Roasted and Washed Concentrate.		Roasted and Washed Concentrate, Calc. on Raw.		Roasted and Washed Concentrate.		Calculated on Raw Concentrate.	
	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.
1	3.90	0.99	4.02	1.02	3.16	0.80	0.13	0.77	0.10	0.60
2	3.89	0.90	4.00	0.94	3.30	0.76	0.06	0.72	0.05	0.59
3	3.95	0.98	4.04	1.00	3.35	0.83	0.07	0.79	0.06	0.66
4	4.05	1.01	4.10	1.02	3.44	0.86	0.09	0.86	0.08	0.72
5	4.06	1.03	4.16	1.06	3.46	0.88	0.08	0.82	0.07	0.68
6	3.96	1.01	4.00	1.02	3.36	0.86	0.07	0.82	0.06	0.69
7	3.91	0.95	4.06	0.98	3.39	0.82	0.06	0.72	0.05	0.60
8	3.97	1.04	4.08	1.06	3.48	0.91	0.055	0.64	0.05	0.55
9	3.97	0.88	4.16	0.92	3.49	0.77	0.08	0.58	0.07	0.49

Test No.	Lost in Roasting and Washing Per Ton of Raw Conc.		Days under Cyanide.	Extraction.				Recovery.	
				On Roasted and Washed Concentrate.		Calc. on Raw Concentrate.		Calc. on Raw Concentrate.	
	Gold, oz.	Silver, oz.		Gold, %.	Silver, %.	Gold, %.	Silver, %.	Gold, %.	Silver, %.
1	0.34	0.09	4	96.8	24.5	97.1	32.6	87.4	22.5
2	0.20	0.13	4	98.5	23.4	98.6	22.5	92.9	19.1
3	0.15	0.06	4	98.2	21.0	98.3	25.8	94.0	19.1
4	0.06	0.03	4	97.8	15.7	97.7	19.1	96.0	15.7
5	0.04	0.01	3	98.1	22.6	98.0	23.6	96.9	22.5
6	0.14	0.03	3	98.2	19.6	98.3	22.5	94.3	19.1
7	0.11	0.07	3	98.5	26.5	98.6	32.6	95.4	24.7
8	0.02	...	3	98.7	39.6	98.6	38.2	98.0	40.4
9	0.01	0.12	3	98.1	37.0	98.0	44.9	97.7	31.5

drying and before roasting, through a ball-mill or similiar pulverizer.

A bottle-test made on a scale of 100 gm. on a sample of roasted concentrate from the above reverberatory charge showed the following results:

TABLE IV

Copper extracted per cent of raw concentrate	
By water-wash	0.435
By cyanide	0.039
Total	0.474
Cyanide consumed per ton of washed concentrate	5.03 lb.
Cyanide consumed per ton of raw concentrate	4.21 lb.
Under cyanide treatment	3 days

1 ton raw concentrate = 0.837 ton washed.

	Gold, oz.	Silver, oz.
Assay of roasted concentrate	3.70	0.86
Assay of washed concentrate	3.90	0.94
Assay of washed concentrate calculated on raw concentrate	3.26	0.79
Loss per ton of raw concentrate	0.24	0.10
Residue assay on washed concentrate	0.05	0.60
Residue assay calculated on raw concentrate	0.04	0.50
	%	%
Extraction on roasted and washed concentrate	98.7	36.2
Extraction calculated on raw concentrate	98.9	43.8
Recovery calculated on raw concentrate	92.0	32.6

The loss shown in this test seems to be mostly mechanical due to dust carried off while stirring the charge; it could probably be much reduced by using a suitable roaster with revolving rabbles and a dust-chamber.

Agitation Tests

The following tests were made in small tanks fitted with wooden paddles.

No. 1. Agitated with cold water, washed by settlement and

TABLE V

Tests Made by Agitation and Decantation

	No. 1.	No. 2.
Weight of roasted concentrate taken	100 lb.	50 lb.
1 ton raw concentrate = after roast (ton)	0.876	0.876
1 ton raw concentrate = after wash	0.837	0.837
Dilution of pulp in water-washing	3:1	3:1
Total preliminary water-wash used per ton (tons)	2.37*	10.7
Copper extracted per ton of roasted concentrate	?	8.04 lb.
Lime added per ton	30 lb.	30 lb.
Cyanide strength used (KCN)	0.25%	0.25%
Cyanide consumed per ton of roasted concentrate	2.36 lb.	4.58 lb.
Cyanide consumed per ton of raw concentrate	2.06 lb.	3.83 lb.
Dilution of pulp in cyanide treatment	3:1	3:1
Time of cyanide treatment (days)	3	5
Total solution used per ton of ore (tons)	4	3.8

* Additional wash given on filter.

	Test No. 1.		Test No. 2.	
	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.
Assay of raw concentrate	3.50	0.89	3.50	0.89
Assay of roasted concentrate	3.70	0.86	3.70	0.86
Assay of roasted and washed concentrate	3.90	0.94	3.90	0.94
Roasted and washed, calculated on raw concentrate	3.26	0.79	3.26	0.79
Residue of roasted and washed concentrate:				
(*a*) After cyanide	0.11	0.55	0.08	0.56
(*b*) Calculated on raw concentrate	0.09	0.46	0.07	0.47
Residue sample with extra wash in laboratory:				
(*a*) On roasted concentrate	0.06	0.54	0.04	0.53
(*b*) Calculated on raw concentrate	0.05	0.44	0.03	0.44
Extraction by cyanide:	%	%	%	%
Calculated on residue as discharged (*a*)	97.2	41.5	97.9	40.4
Calculated on residue as discharged (*b*)	97.4	48.3	98.0	47.2
With extra wash (*a*)	98.5	43.6	99.0	43.6
With extra wash (*b*)	98.6	50.6	99.1	50.6
Recovery based on raw concentrate†	90.6	37.1	91.1	36.0
Recovery with extra wash	90.7	39.3	92.3	39.3

† In calculating "recovery" allowance is made for losses of gold and silver in roasting.

TABLE VI

Tests Made by Percolation

	No. 1.	No. 2.
Weight of roasted concentrate taken	100 lb.	32 lb.*
Total preliminary water-wash used per ton of roasted concentrate (tons)	3.48	3.92*
Lime added per ton (lb.)	30	26
Strength of solution used (KCN)	0.25%	0.25%
Cyanide consumed per ton of roasted concentrate (lb.)	6.48	2.77
Cyanide consumed per ton raw concentrate (lb.)	5.44	2.32
Solution used per ton of roasted concentrate (tons)	2.63	1.46
Final water-wash per ton of roasted concentrate (tons)	0.92	0.41
Time of cyanide treatment (days)	3	5
Depth of charge for percolation (inches)	2½	10

* Hot water used, and ore charged into tank while hot (200° F.).

	Test No. 1.		Test No. 2.	
	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.
(*a*) Residue of roasted and washed concentrate after KCN	0.65	0.70	3.00	0.77
(*b*) Residue calculated on raw concentrate	0.54	0.59	2.51	0.64
After extra wash in laboratory (*a*)	0.22	0.62	2.18	0.78
After extra wash in laboratory (*b*)	0.18	0.52	1.82	0.65
	%	%	%	%
(*a*) Extraction on roasted concentrate	83.3	25.5	23.1	18.1
(*b*) Extraction calculated on raw concentrate	84.6	33.7	28.3	28.1
After extra wash in laboratory (*a*)	94.4	34.0	44.1	17.0
After extra wash in laboratory (*b*)	94.9	41.6	48.0	28.0
Recovery based on raw concentrate	77.7	22.5	21.4	16.9
Recovery after extra wash	88.0	30.3	41.1	15.7

TABLE VII

WEIGHT OF UNITED CHARGE, 200 LB.

Extra washes:	Tons.
A. Water per ton of charge	1.9
B. Solution, 0.147% KCN, per ton of charge	0.4
C. Water per ton of charge	2.3
	4.6

Additional cyanide consumed per ton of charge in treatment B (lb.) 0.82
Total time for additional treatment ..... 3 days

UNITED CHARGES FROM PERCOLATION AND AGITATION TESTS, AFTER ADDITIONAL WASHING

(1) After further water-washing A.
(2) Same with extra water-wash in laboratory.
(3) After final cyanide-wash B and water-wash C.
(4) Same with extra water-wash in laboratory.

	(1)		(2)		(3)		(4)	
	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.
Residue on roasted concentrate	0.07	0.59	0.06	0.62	0.06	0.59	0.05	0.60
Residue calculated on raw concentrate	0.06	0.49	0.05	0.52	0.05	0.49	0.04	0.50
	%	%	%	%	%	%	%	%
Extraction on roasted concentrate	98.2	37.2	98.5	34.0	98.5	37.2	98.7	36.2
Extraction calculated on raw concentrate	98.3	44.9	98.6	41.6	98.6	44.9	98.9	43.8
Recovery calculated on raw concentrate	91.4	33.7	91.7	30.3	91.7	33.7	92.0	32.6

TABLE VIII

Tests on Influence of Cyanide Strength

Charge for each test: roasted and washed, 100 gm.; lime, 1 gm. = 20 lb. per ton; solution, 300 c.c. = dilution 3:1.
Time under cyanide treatment ..... 4 days
Weight of 1 ton raw concentrate after roast ..... 0.865 ton
Weight of 1 ton after roast and wash ..... 0.811 "

	Gold, oz.	Silver, oz.
Assay of raw concentrate	4.88	1.12
Assay of roasted concentrate	5.35	1.24
Assay of roasted and washed concentrate:		
1st series	5.72	0.82
2d series	5.68	1.32
Assay of roasted and washed concentrate calculated on raw concentrate:		
1st series	4.68	0.67
2d series	4.61	1.07

Test No.	Copper Extraction Per Cent of Raw Concentrate.			Strength of Cyanide Used, KCN, %	Cyanide, lb., Consumed.		Residue Assays.			
	By Water-Wash, %	By Cyanide, %	Total, %		Per Ton of Roasted and Washed Concentrate.	Per Ton of Raw Concentrate.	On Roasted and Washed Concentrate.		Calculated on Raw Concentrate.	
							Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.
Series No. 1:										
1	0.364	0.026	0.390	0.50	6.26	5.12	0.09	0.63	0.074	0.52
2	0.364	0.024	0.388	0.25	3.18	2.60	0.01	0.63	0.082	0.52
3	0.364	0.027	0.391	0.125	2.30	1.88	0.10	0.61	0.082	0.50
4	0.364	0.022	0.386	0.062	2.36	1.93	0.11	0.62	0.09	0.51
Series No. 2:										
5	0.411	0.034	0.445	0.50	6.20	5.03	0.08	0.66	0.065	0.54
6	0.411	0.036	0.447	0.25	4.42	3.58	0.08	0.68	0.065	0.55
7	0.411	0.040	0.451	0.125	3.19	2.59	0.095	0.71	0.077	0.58
8	0.411	0.038	0.449	0.062	3.44	2.79	0.10	0.72	0.08	0.58

TABLE VIII—(*Continued*)

Series No.	Test No.	Extraction on Roasted and Washed Concentrate.		Extraction Calculated on Raw Concentrate.		Recovery Calculated on Raw Concentrate.	
		Gold, %	Silver, %	Gold, %	Silver, %	Gold, %	Silver, %
1	1	98.4	23.2	98.5	53.4	94.4	13.4
	2	98.3	23.2	98.3	53.4	94.2	13.4
	3	98.3	25.6	98.3	55.4	94.2	15.2
	4	98.1	24.4	98.2	54.5	94.1	14.3
2	5	98.6	50.0	98.6	51.8	93.1	47.3
	6	98.6	48.5	98.6	50.9	93.1	46.4
	7	98.3	46.2	98.4	48.2	92.9	43.7
	8	98.2	45.5	98.4	48.2	92.8	43.7

TABLE IX

EFFECT OF VARYING TIME OF TREATMENT

Charge for test as in Tests Table VIII

1 ton roasted concentrate = 0.919 ton after water-wash.

	Gold, oz.	Silver, oz.
Assay of roasted concentrate	4.05	2.45
Assay of roasted and washed	4.52	2.64

	Gold, oz.	Silver, oz.
Calculated assay of roasted	4.15	2.43

Strength of solution maintained at 0.1% KCN.

	Test No. 1.	Test No. 2.
Time of cyanide treatment (hours)	28	71
Cyanide consumed per ton treated (lb.)	1.50	3.70

	Test No. 1.		Test No. 2.	
	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.
Residue of roasted and washed concentrate	0.095	1.73	0.09	1.61
Residue calculated on roasted concentrate	0.087	1.59	0.083	1.48
	%	%	%	%
Residue of roasted and washed concentrate	97.9	39.8	98.0	43.9
Extraction calculated on roasted concentrate	97.9	35.1	98.0	39.6

decantation, then drained by vacuum on a horizontal filter-tray; re-pulped with lime and cyanide solution.

No. 2. Agitated with hot water, washed by settlement and decantation, neutralized with lime and agitated with cyanide without previous filtration. Cyanide treatment by decantation, finally washing with water.

Percolation Tests

Portions of the same roasted charge as were used for the previous tests were leached in tanks with a canvas filter, using vacuum to aid filtration. After washing out soluble salts as far as possible in this way, the residue was mixed with lime and treated by percolation with cyanide solution in the same manner.

In view of the unsatisfactory results obtained by percolation and the fact that further extraction was made by increased water-washing, the residue of charge No. 1 was mixed with the residue of charge No. 1 treated by agitation (see Table V) and the united charge agitated further with water, then with weak cyanide solution, and finally with water again.

The result of these tests indicates that thorough washing is essential for a high extraction. Filtration without vacuum was found to be practically impossible.

The following tests were made on another portion of roasted concentrate, to determine the influence of cyanide strength on extraction. Eight tests were made; in the first four a preliminary wash was given with hot salt solution, 10% NaCl, using 2 tons of material treated. In the remaining four tests the preliminary wash was given with water alone, using 4 tons per ton of material. The salt-wash showed some extraction of silver, but it does not appear that any advantage derived from this would warrant the additional cost.

The cyanide treatment is detailed in the accompanying tables:

From these results it appears that the extraction is scarcely affected by variation of cyanide strength within the limits and under the conditions of the tests. The cyanide consumption,

TABLE X

	Test No. 1.		Test No. 2.		Test No. 3.	
Weight of roasted concentrate treated (gm.)	150		125*		150	
1 ton raw = roasted (ton)	0.801		0.788		0.854	
1 ton raw after chlorination	?		?		0.834	
	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.
Assay of raw concentrate	4.92	1.14	4.92	1.14	3.50	0.89
Assay of roasted concentrate	6.24	1.28	6.18	1.30	3.87	1.09
Roasted concentrate, calculated on raw	5.00	1.03	4.87	1.02	3.30	0.93
Residue of roasted, after chlorination	0.14	1.32	0.15	1.33	0.12	1.08
Residue calculated on raw	0.11	1.06	0.12	1.05	0.10	0.90
Actual recovery by precipitation with $FeSO_4$:						
Per ton of roasted	6.09	....	5.49	....	3.84	....
Per ton of raw	4.88	....	4.27	....	3.28	....
Extraction.	%	%	%	%	%	%
On roasted concentrate	97.8	....	97.6	....	97.1	0.9
Calculated on raw	97.8	7.0	97.6	7.9	97.1	....
Recovery from raw concentrate:						
(*a*) Based on residue assays	99.4	....	96.5	....	91.4	....
(*b*) Based on $FeSO_4$ precipitation	99.2	....	86.9	....	93.6	....

* Ground to pass 200-mesh before chlorination.

however, increases with increasing strength. Apparently the best results are obtained with a strength of 0.125% KCN.

Two tests were also made on another portion of roasted concentrate from the same lot of ore to determine the influence of time on the cyanide treatment.

From this test it is evident that the gold in the roasted concentrate is rapidly soluble in cyanide. The small insoluble portion seems to be quite unamenable to prolonged treatment or to stronger solutions.

The foregoing tests sufficiently indicate that the San Sebastian concentrate, produced by flotation, may be treated successfully on a commercial basis by the method of roasting, water-washing, and cyaniding. Some tests were, however, made by alternative methods for the purpose of comparison.

The processes thus tried were:

1. Chlorination by saturating the roasted charge with chlorine gas and leaching with water, as in the old Plattner process.

2. Direct cyanide treatment of the raw ore after fine grinding in a tube-mill with steel balls.

Chlorination Tests

A charge of roasted concentrate was moistened with about 15% of water, and placed loosely, without any paper or other filter, in a porcelain funnel with flat perforated diaphragm. Chlorine gas was introduced from below through the neck of the funnel, and, after saturation, the charge was allowed to stand covered for 24 hours. It was then leached out with water and the residue dried and assayed. The extraction was found by difference of head and tail assays; it was also checked by precipitating the filtrate with ferrous sulphate, allowing to settle and collecting the deposited gold on a filter. This was dried and cupelled.

In one case the residue after chlorination was further treated by agitation with cyanide. The results obtained by chlorination are detailed in the accompanying table.

The residue from test No. 3 (Table X) was further treated by cyanide, by agitation for 4 days with a solution originally at 0.2% KCN, and increased toward the end of the treatment to 0.5% KCN, using a dilution of 3 : 1. This treatment yielded the following results:

	Gold, oz.	Silver, oz.
Final residue after cyanide treatment	0.07	0.87
	%	%
Extraction from chlorination tailing	41.7	19.4
Total extraction from raw concentrate	98.3	18.4

From these figures it would seem that the results to be expected from chlorination, or from chlorination followed by cyanidation, are in no way superior to those obtained by water-washing and cyanidation. Either method will give satisfactory extraction and the choice would depend on relative cost under local conditions.

Direct Cyaniding of Raw Ore

It is interesting to compare the results obtained on this ore by direct cyaniding without any form of concentration, with those given by the combination of flotation and cyanidation.

The following tests were made on portions of the same lot of ore as was used for tests detailed in the preceding tables. Three charges were treated; the first two were taken from a portion crushed in a small tube-mill with manganese-steel balls, using the following quantities:

Ore, 25 lb.; lime, 0.25 lb.; water, 17 lb.

Time of grinding, 6 hours.

The pulp was drained on vacuum-filter to 26.4% moisture.

The third test was made on part of a larger portion of ore crushed in the same manner, but in a larger mill, for use with a 200-lb. flotation machine.

TABLE XI

DIRECT CYANIDING OF RAW ORE, WITHOUT CONCENTRATION

	Test No. 1.	Test No. 2.	Test No. 3.
Wet weight of ore taken (gm.)	708	708	100
Dry weight of ore taken (gm.)	521	521	95
Solution added (c.c)	1,457	1,457	300
Lime added, per ton of ore (lb.)	....	....	21.1
Strength of solution maintained, KCN	0.1%	0.2%	0.2%
Final dilution of pulp	3:1	3:1	3:1
Time under cyanide treatment (days)	5	5	3
Cyanide consumed per ton of ore (lb.)	4.80	6.32	4.76

	Test No. 1.		Test No. 2.		Test No. 3.	
	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.	Gold, oz.	Silver, oz.
Head assay	0.625	0.16	0.625	0.16	0.895	0.13
Residue assay	0.205	0.07	0.16	0.04	0.155	....
Extraction (%)	67.2	56.2	74.4	75.0	82.7	....

CYANIDE TREATMENT OF FLOTATION TAILING

A flotation test was made on the ore used in Test No. 3 (Table XI), resulting as follows:

Product.	Weight, %	Assay Value.		Percentage of Total Value.	
		Gold, oz.	Silver, oz.	Gold.	Silver.
Head	.....	0.895	0.13	....	....
Concentrate	12.45	6.53	1.04	90.8	99.6
Middling	11.45	0.35	....	4.5	....
Tailing	76.10	0.055	....	4.7	....

The tailing thus produced was agitated with cyanide, with results as shown below:

TABLE XII

CYANIDE TREATMENT OF RAW FLOTATION TAILING

Wet weight of tailing taken, 100 gm.
Moisture, 7.4%. Dry weight, 92.6 gm.
Lime added, 1 gm. = 21.6 lb. per ton of tailing.
Strength of solution maintained at 0.2% KCN.
Dilution of final pulp, 3 : 1.
Time under cyanide treatment, 3 days.
Cyanide consumed per ton of tailing, 1.40 lb.

	Gold, oz.
Assay before cyaniding	0.055
Assay after cyaniding	0.0125
Extraction	77.3%

COMPARISON OF METHODS

For the sake of comparison, we may assume in view of previous results that an extraction of 98% could be obtained from the concentrate yielded by the above flotation-test, by the method detailed, namely, roasting, water-washing, and cyaniding. The values shown in the middling may be eliminated on the assumption that in practice the middling would be constantly returned to the head of the machine, and that finally only two products would be obtained, concentrate and tailing, having the same assay-values as in the test. The result of the flotation-test would then appear as follows:

Product.	Weight, %	Assay Value.		Percentage of Total Value.	
		Gold, oz.	Silver, oz.	Gold.	Silver.
Concentrate	12.97	6.53	1.04	94.6	103.8
Tailing	87.03	0.055	....	5.4	.....

We have, therefore, per ton of raw ore:	Gold, oz.	Gold.	Percentage of Total Gold.
Recovered from concentrate:			
$6.53 \times 0.1297 \times 0.98 =$	0.830	$17.16	92.7
Recovered from tailing:			
$0.055 \times 0.8703 \times 0.773 =$	0.037	0.76	4.1
Total recovery	0.867	$17.92	96.8
Heads	0.895	18.54	100

Taking the figure of Test No. 3 (Table XI) as indicating the possible recovery by direct cyanide treatment we have:

	Gold, oz.	Gold.	Percentage of Total Gold.
By direct cyaniding	0.74	$15.30	82.7
Additional recovery by combined method	0.127	2.62	14.1
		Per ton of concentrate.	
Flotation, 16c. per ton of ore $= \frac{0.16 \times 100}{13} =$		$1.25	
Roasting		1.00	
Extra labor, etc., in cyaniding		0.50	
		$2.75	
Per ton of raw ore, $2.75 \times 0.1297 =$		0.36	
Net saving by combined method		2.26	

In addition to this there is a saving in cyanide consumption as follows, per ton of raw ore:

	Cyanide Consumed.
By direct treatment	4.76 lb.
By combined treatment:	
Concentrate (say, 5 lb. per ton) $5 \times 0.13 =$	0.65 lb.
Tailing, $1.4 \times 0.87 =$	1.12
	1.77

showing a saving in cyanide of 2.99 lb.; taking cyanide at 16c. per lb. of KCN equivalent, this would amount to 48c. per ton of raw ore treated, bringing the total saving to $2.74 or about $9600 on a monthly output of 3500 tons.

The tests given in Table III show that about 0.4% of copper, or 8 lb. per ton of raw concentrate (in this case 2 lb. per ton of raw ore) can be extracted in a soluble form, and might be recovered as an additional source of revenue.

DISPOSAL OF FLOTATION RESIDUE[1]

By W. Shellshear

Introduction.—There are many methods of handling sand and slime from metallurgical operations, but in this article the draining and conveying of waste products from flotation processes will be specially dealt with, the methods given being those in use at the leading flotation plants in Australia.

Draining and De-watering.—It is generally advisable to thoroughly de-water the residue from flotation treatment in order to form a closed circuit of liquor. This maintains constant conditions throughout the plant and avoids waste of oil, which would be carried away by the solution with the tailing. The methods that may be used for this purpose are:

(*a*) Filtering in vats; (*b*) combination of a submerged draining-belt and Dorr thickeners; (*c*) combination of Caldecott diaphragm-cones, draining-belt, and Dorr thickeners, and (*d*) combination of Dorr classifiers and Dorr thickeners.

Filtering in Vats.—In this system, shown in Fig. 2, the pulp from flotation is run direct into vats. These are usually 15 ft. diam., their depth varying from 10 to 20 ft. In the centre of each, and before filling, a tube or pipe, 15 in. diam., that fits over the circular discharge-hole, is inserted. When the vat is ready for emptying, this tube is lifted out, a large proportion of the tailing falling through the centre hole onto a conveyor underneath. The remainder is afterward shoveled upon the same conveyor.

A wooden frame, not shown in the sketch, is erected above the vat to support the lifting-device, a screw-block being used

[1] From the *Mining and Scientific Press* of December 11, 1915. Abstract from *Min. and Eng. Review*, Melbourne, Australia.

to raise the pipe to the desired height. This operation is afterward carried out by an ordinary block and tackle. The vat may be made of wood or iron, and the height to which it may be con-

FIG. 1.—Australian Boom-Distributer. Belt-driven without gear at 900 ft. per min. by slow-speed motor controlled from below. The machine can be moved while working.

structed is controlled by local conditions, such as the design of the plant, and the nature and fineness of the material to be filtered. It is, however, apparent that the greater the height that can be economically employed, the less the labor required, as a

proportionately larger amount drops through the centre of the vat without shoveling. This would tend to make the inner tube too long to be handled conveniently, but the difficulty has been overcome by making the tube in sections, each of which is lifted in its turn from the top as emptying proceeds.

The time of filtering is arranged according to the number of vats employed, but it is the usual practice to run the pulp through a number in series, so that the slime settles from the solution. Thus, if six vats are in use, one may be draining and another emptying, while the remainder would be used for the pulp flowing, in series, through them. The filtered water is carried off by a number of pipes at the bottom of each vat. Under certain conditions a suction-pump is connected to these pipes to assist the filtering, but this is not the usual practice. As a filtering medium, cocoa-nut matting is used generally.

After a vat has been emptied, the tube is dropped into the discharge-hole, two lugs, one on each side, keeping it in position. The open space around the tube is then filled with clay. It is advisable to have the bottom of the vat six feet above the ground-level to allow of easy access to the conveyor underneath. At the spot where the sand is discharged upon the conveyor-belt, guide-doors are arranged parallel with the belt to prevent sand going over its edge, and the number of idlers under the conveyor is increased to prevent it sagging under a rush of feed. The conveyor is usually a flat belt, 24 in. wide, traveling at 350 to 450 ft. per minute, 4-in. iron idlers being used.

This method has many excellent features; its advantages are: (1) The moisture of the drained tailing is less than in any other system; (2) the slime is drained at the same time as the sand; (3) dams for handling the slime and the cost of labor on same are eliminated; (4) dusting troubles are minimized on the dump, owing to the slime helping to set the tailing; (5) the angle of repose of the dump is increased, thus enabling more sand to be stacked per unit of ground-area; (6) no trouble with conveyors handling tailing will cause a stoppage in the main plant; (7) accurate sampling of products is possible, enabling shift-work to be kept under control.

The disadvantages are: (1) High initial cost of erection; (2) relatively high cost of labor in emptying vats; (3) clari-

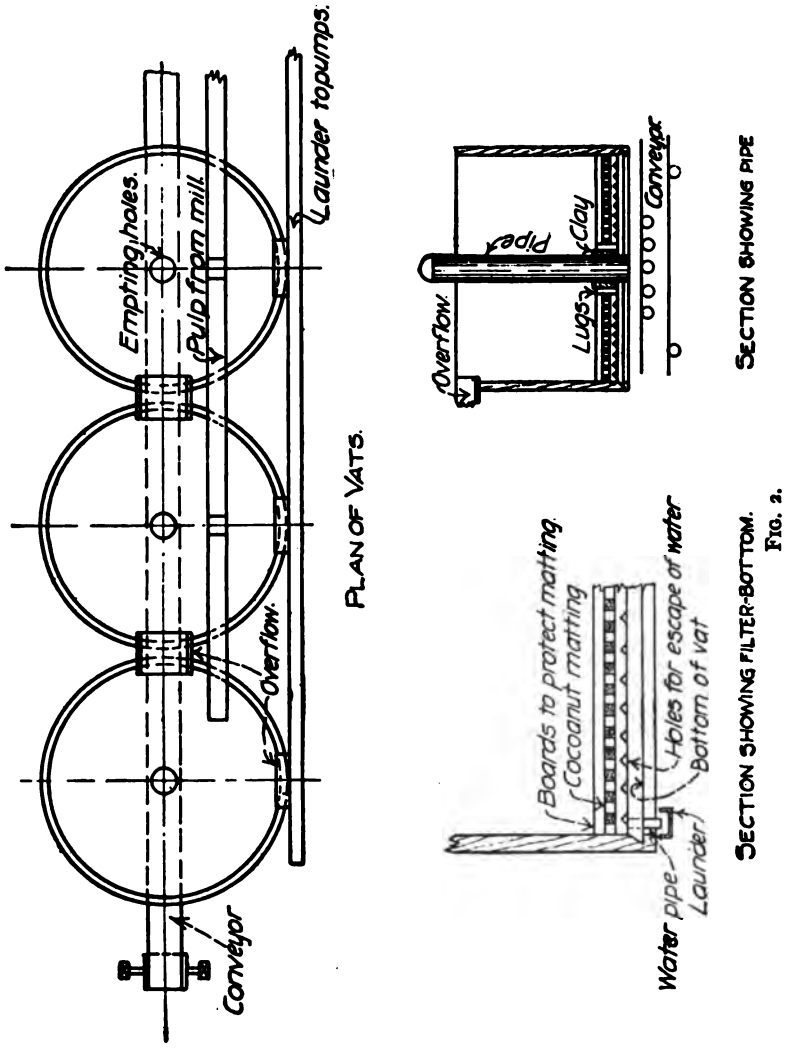


FIG. 2.

fication of solution is not usually as complete as is the case with other methods.

Combination of Draining-Belt and Thickeners.—The idea of the submerged draining-belt, I think, was first introduced in

connection with the Elmore process in order to overcome the difficulty of discharging the residual pulp without upsetting the vacuum in the flotation apparatus. In this system the belt runs inside an iron trough filled with water, being forced into a semicircular shape by means of a spherical pulley, as shown in sketch, Fig. 3. The belt travels under water for a certain distance, rising at a slope of 15 to 20° onto the head-pulley.

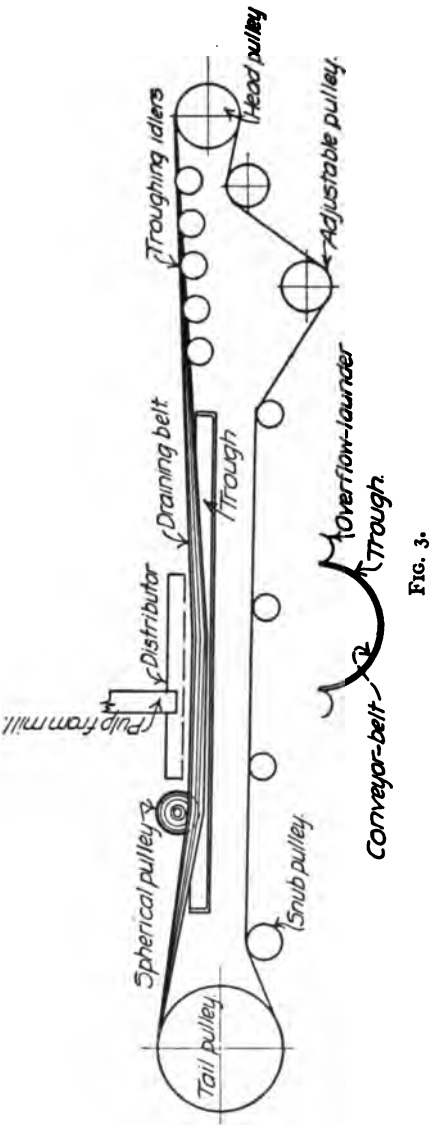


FIG. 3.

The drive is usually from the tail-end by means of a worm-wheel on the tail-pulley shafting. This tail-pulley is generally 6 ft. diam., and is faced on the outside with wooden boards to give the belt a better grip. The feed is, preferably, distributed to the belt by means of an iron launder with holes in the bottom, wooden guides being arranged to guard against sand getting between the under side of the belt and the trough. The trough has side launders attached to carry the overflow to Dorr thickeners, the number of the latter depending on general conditions such as nature of slime, amount

of water in circulation, etc. The submerged belt forms an excellent de-sliming system, by reason of the classification in the trough; its capacity is 4000 or more tons a week of mixed slime and sand. The draining of the sand is accomplished as it rises from the surface of the liquid in the trough to the head-pulley.

In order to accelerate this draining action, a bumper is usually employed. This consists of an idler driven by two eccentrics. The vibration caused on the belt by the idler striking it underneath displaces a larger quantity of water from the sand, and thus reduces the proportion of moisture in the final product. An iron scraper is used for removing the tailing from the draining-belt; it may be kept under pressure by means of iron springs. This method is very good, especially where the room available for drainage is limited. It is also convenient where the height of the flotation plant above the ground is small.

The life of the belt is less than that of an ordinary draining-belt, owing to the heavy pressure of the spherical roller, and the action of the hot circuit-liquors in which the belt is submerged. The labor for attendance is small. This method is at present in use on two of the large flotation plants at Broken Hill.

Combination of Cones, Draining-Belt, and Thickeners.—This method, diagrammatically illustrated in Fig. 4, has been installed in the latest flotation plant at Broken Hill. The size of the Caldecott cones usually employed is 12 ft. diam. and 10 ft. deep, the diaphragm being 2 ft. to 2 ft. 6 in. from the bottom of the cone. In most cases a plate-diaphragm is used, but the introduction of an iron ball to serve the same purpose has been most successful. Where a cone of this type is used as a thickener, rather than as a slime-classifier, more pulp may be thickened, as the height of pulp need not be so finely adjusted. Still, it is customary to keep the level of the sand two feet from the top of the cone, as measured in the centre. The feed usually passes into these cones through a centre of the Callow type.

To remove the thickened pulp continuously and divert it onto the draining-belt, an ordinary plug may be used with advantage, provided coarse rubbish has been removed pre-

viously. Another successful device is a plug-valve or a plug worked from the top, fitting into a seat at the bottom of the cone. The type of draining-belt employed is 36 in. wide. The belt rises gradually, about 1 in 60, from the tail-pulley, the last 30 ft. of the slope being increased to about 20°. The belt-speed is 20 to 30 ft. per min., both ordinary and troughing idlers, of 6 in. diam., being used. As the operation of the belt is slow, wooden idlers working in cast-iron "dead-eyes" can be successfully used for the horizontal idlers, the troughing-idlers being of the usual type.

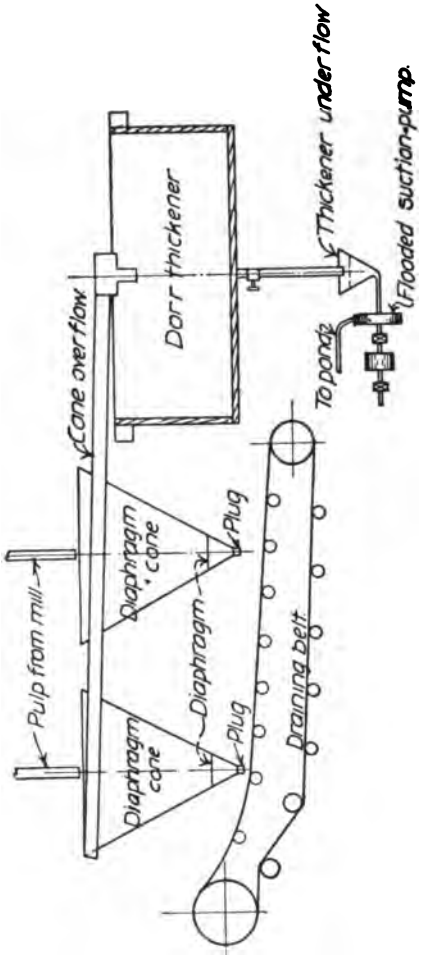


FIG. 4.

The drive is at the head end, double gearing for speed reduction being employed. The head-pulley is generally 5 ft. diam., the snub-pulley 18 in. diam., and arc of contact 200 to 250°. The tail-pulley is usually 2 ft. diam. Rubber belting on the face of these pulleys reduces the slip, thereby increasing the power-efficiency and the life of the belt.

The overflow from the Caldecott cones goes into one or more Dorr thickeners, according to requirements, the underflow from the thickeners, as in other methods, being handled with flooded suction-pumps. Attempts to mix the underflow from the Dorr

thickener with pulp on the draining-belt in order to convey them together to the dump have not so far proved successful. For the control of the underflow from Dorr thickeners the hydrometer method (described in " Rand Metallurgical Practice ") has proved quite satisfactory, a constant pulp, with Broken Hill slime, of 50% solid being easily maintained. This method is considered a good one, because the cost of labor is low, the life of the draining-belt is prolonged, and the cost of maintenance is small. Adequate head-room is, however, necessary for the erection of the cones; in some cases elevation is essential. A disadvantage is that a stoppage of the dump-belts causes a stoppage of the whole plant.

Combination of Classifiers and Thickeners.—This method has not, to my knowledge, yet been adopted at any plant in Australia, but the great success that it has achieved at cyanide plants in America shows that it could be applied to the handling of tailing and slime products at Broken Hill. The usual type of Dorr classifier, however, would have to be especially lengthened to cause extra draining of the sand product. Owing to the regular working of these machines the usual draining-belt may be discarded. At the same time very little head-room would be required. This method is illustrated in Fig. 5, which shows the classifiers delivering direct onto the inclined belt. It has, however, the same disadvantage as the method last mentioned, in that it does not make the treatment-plant independent of the dump-belt stoppages. The cost of erection and maintenance would, however, be small.

Handling of Drained Products.—Tailing may be handled in the following ways: (*a*) Inclined conveyor-belts and boom-stackers, (*b*) aerial trams, (*c*) trucking, and (*d*) sluicing.

Inclined Conveyor-Belts and Boom-Stackers.—The usual angle for an inclined conveyor is 20°; where possible the conveyor should be driven from the head-end. Where the head-end is high above the ground, the drive should be either from the tail-end or from a large centre-pulley, midway along the belt, having a snub-pulley at each side above it, the centre-pulley being 6 to 8 ft. diam. and resting, preferably, on a concrete base.

well to remember that the horse-power lost in friction per 100 ft. varies inversely as the length of the belt, averaging from 2 to 6 hp. per 100 ft. A tightening arrangement is usually fixed on the tail-pulley of this type of belt to cause it to run true and take up any unnecessary slack. When an inclined conveyor has been carried out to an economical distance, the tailing at its end is made into a bed for a boom-stacker. This is an iron pole, which is held in position by four strong guy-ropes. Attached to the pole is an iron lattice-girder, which is supported similarly to a cantilever by guy-ropes attached to the pole itself. This boom-stacker rests on a steel ball in a cup-shaped receiving device, which enables it to swing around as desired. The weight of the boom-stacker is spread over a large area by means of a number of heavy timbers resting in the prepared foundation on the dump. The conveyor on the boom-stacker is driven by a motor fixed behind the boom, and traveling around with it. [The photograph (Fig. 1) shows a good boom-stacker at Kalgoorlie, Western Australia, from which place the Broken Hill system was largely copied.—EDITOR.]

Aerial Trams.—These are so well known that they need no description here. For moderate tonnage they are seldom used, as a bin is required and two men loading and operating trucks.

Handling of Slime.—The pulp from Dorr thickeners is either transferred by flooded-suction centrifugal pumps or three-throw pumps, or else elevated by an ordinary belt-elevator. Where there is room for a slime-dam close to the treatment-plant, the belt-elevator, which is a very economical system of elevation, may be used. In other cases centrifugal pumps are resorted to. The thickened pulp may also be delivered to dams or sprayed onto the surface of sand-dumps. To remove the drained water it is preferable to use a wooden box-launder. This consists of two box-launders connected in the form of a right-angle, and fixed in position at the starting of the building of the dam. The horizontal portion of the launder is laid 12 ft. inside the dam, and is carried to the water-sump outside it. The vertical portion passes through the slime and is bored with holes, which are plugged from the bottom upward as the building of the dam pro-

ceeds. Probably the best method of handling slime-pulp is to pump it through a nozzle onto the surface of sand-dumps. By such means it may be sprayed evenly all over the dump. This does away with dams, and checks the dust rising from the sand-dump. The idea was first originated in South Africa, and has only lately been introduced into Australia.

FLOTATION PRINCIPLES[1]

By C. Terry Durell

In attempting to start a discussion on flotation by setting forth my osmotic hypothesis, the main objects were (1) to firmly establish fundamental laws and definitions and (2) to bring out and classify new phenomena. Flotation terms have been misused and jumbled in the same way that the so-called expert makes a mining report ridiculous by the use of geological terms. Litigation has made the subject more confusing, and it is still an indefinite cloud to most people. Now that first principles and definitions are being agreed upon, concerted effort is starting experimentation along definite lines that will lead to far-reaching results instead of the heretofore duplication of efforts leading to nothing. Before the final solution of a problem can be accomplished, the problem must be stated properly. It is therefore quite gratifying to see that the discussion is fulfilling the two main purposes and that the flotation problem now stands out more clearly.

A man can never learn from one who agrees with him entirely. For this reason I was pleased to see exceptions taken to my article "Why Is Flotation?" O. C. Ralston thinks I used rather loosely the two words "nascent" and "occlusion." It took me a long time to realize the prime essential for an effective froth. This can only be described clearly by the word "nascent." It also required several years of patient effort to convince myself that the whole subject depends on gas "occlusion."

Being unable to learn anything more in this country concerning flotation, some four years ago I made a trip to Australia, the home of flotation. There I saw for the first time copper con-

[1] From the *Mining and Scientific Press* of February 19, 1916.

centrate won by flotation. At the Lake View Consols, in the Kalgoorlie district, I saw one of the old bulk-oil flotation plants.

It was at Broken Hill, however, that I had plenty of time and opportunity to study flotation. Companies using different processes were naturally adverse to entertaining a stranger who might be gathering information to be used against them in one of the various law-suits. As soon as the managers or officials in charge were assured that I was not there for that purpose, they afforded me ample opportunity to learn everything concerning flotation, giving me access to figures and data. In this country it is seldom that a comparative stranger receives such courteous treatment as was shown me by the cordial company officials there.

At the Proprietary mine, where the Delprat process was in operation, no oil was being used, yet there was practically the same persistent froth as at other plants using the Minerals Separation process. This fact then eliminates the two hypotheses for flotation advanced by Mr. Ralston,[2] who says that "The first hypothesis is based on some academic work done by Reinders, who deduced the following inequalities as applying to a case where a powder, or the particles of a colloid, is suspended in a liquid to which is added a second liquid that is immiscible with the first." There at the Proprietary mine, where 500 tons per day was being treated by a single "cell," no such liquid was used. Therefore, according to Mr. Ralston's hypothesis, froth-flotation could not take place. Yet the records show that thousands of tons of zinc concentrate has been recovered by froth where no oil was used. I quite agree with Mr. Ralston when he says, "It hardly needs to be said that here we find something very close to the conditions obtained in the flotation process." "In fact, the old Elmore bulk-oil flotation method fulfills exactly the conditions that Reinders had in mind." By basing the whole subject of flotation on gas occlusion, as I have done in my article, "Why Is Flotation?" in the *Mining and Scientific Press* of September 18, all flotation processes may readily be explained.

[2] "Why Do Minerals Float?" by O. C. Ralston, *M. & S. P.*, Oct. 23, 1915.

On seeing for the first time a single spitzkasten being fed 700 lb. of ore per minute by means of a "push-feeder" as is done at the Proprietary, one can but marvel at the simplicity and rapidity of action of this froth-flotation process, which makes a marketable zinc concentrate with high recovery without retreating. As no oil was used, I summed up as follows the essential elements: gas, acid, and heat, in addition to ore and water. There is nothing else essential to this treatment. Studying the conditions there, I soon became convinced that the function of the acid was not only to produce bubbles for froth-formation, but also for the creation of selective action. Since the solution was kept as near the critical temperature of 80° C. as possible, no air from the solution could aid in froth-formation, because the solution was under a hydrostatic head and was admitted at the bottom of the spitzkasten instead of by means of a jet above the surface. It was easily seen that the function of gas was for froth-formation and that the persistence of the bubbles was mainly due to the enveloping net of mineral particles. What then was the function of the heat? The cold ore dropping into this hot solution carried some air with it which the heat expelled. This was not the essential factor. The heat expelled enough of the occluded gas from the ore particles to form nuclei for the attachment of nascent gas to form flotation bubbles.

Studying the Elmore vacuum process at the British Broken Hill plant at a later date, I summed up the essential elements there as follows: vacuum (to liberate the air) acid, oil, and alkali. At a first glance it was seen that here was another method of making bubbles and froth. This froth was perhaps more persistent, as the envelope for the bubbles seemed tougher. The difference was so slight that it is best described as that between the froth formed during the early stage of the clean-up in the acid or "cutting-down" tank of a cyanide plant and the froth formed during the later stages. It was natural, therefore, to assume that the principle or cause of this Elmore process of flotation was identical with that of the Delprat at the Proprietary. I was told there, and have been repeatedly told since, that the oil was the cause of the selective action. I never will believe

this, with all the evidence against it, although on account of adsorption—not occlusion—of gases by the ore particles, they are more easily wetted with oil than with water. The results at these two mines were practically the same. The grade of the concentrate at the British plant was higher, by reason of mechanical refinements, and not the difference in process. Therefore the oil could not be the essential element for selective action, because no oil was used at the Proprietary. The oil was an essential element only in that it toughened the froth. Owing to mechanical means of operation, the froth could not be removed so quickly nor could it be carried in such a deep layer. Therefore oil was added to toughen it. Using Mr. Scott's words,[3] "This froth rises and floats much the same as a board would" while the Delprat bubbles "float over, if we get them over before they break"; and "if they do break, the mineral drops and is caught by the bubbles below." Oil, then, can be eliminated in making the following comparison between the essential elements of these two processes. Acid creates the selective action as in the Delprat method; lime is then added to neutralize it, because the vacuum machines are of cast-iron. Acid was found to be necessary in the Delprat process to create the bubbles. It was necessary for these bubbles to form as they "came into being" on mineral particles as nuclei. Nascent bubbles of air are formed in the same way, so that the vacuum of the Elmore process takes the place of the acid in the Delprat.

At the British plant, in making a froth, the solutions were not heated, for the reason that the vacuum which drew the dissolved air from the liquid, in accordance with the law of Henry, also drew a sufficiency of occluded air from the mineral particles to form nuclei for the air "coming into being" from the liquid. The acid had already acted as previously described. The small slow-speed mixer, just ahead of the vacuum machines, used for stirring oil into the thickened pulp, could in no way super-saturate the mass with air as is the case with a Minerals Separation machine, which process will be taken up later.

[3] Walter A. Scott, counsel for defendant in the case of Minerals Separation v. Miami.

When I began the study of the De Bavay process at the Amalgamated Zinc plant, I was at a loss, at first, to see how the same principles underlying the other two processes just mentioned could apply there. The following essential elements were separated out: gas (in the form of air), acid, and oil. Mr. Meredith told me the object of the acid was to clean the mineral particles. While it undoubtedly does this, my contention is that it acts as an electrolyte, as I have described, to create the selective action afterward manifest during the oiling and aerating stages of the process.

Oiling of the mineral particles is the next stage and can only take place in liquid pulp, as I have explained, when particles themselves contain gas. It required a careful study of the apparatus at the Amalgamated plant before I was able to understand that the same underlying principles applied here. Air was necessary; yet where and how was it introduced? This is best described in T. J. Hoover's[4] words: "Throughout this manipulation, including the acid-washing, the oiling, the raising with compressed air, and the flowing over the corrugated cone, the sulphide particles are repeatedly aerated, and as a result, especially after the oiling, take up their adhesive air-films and float." They were not using corrugated cones when I was there. Instead, the cones were covered with concentric rows of staggered triangular obstructions. These were made by bending the triangular burrs from holes punched in galvanized sheet-iron cones until they were perpendicular to the surface. These cones were then fitted down tightly over similar cones not punched. A montejus was used to lift the prepared pulp to these cones. As Mr. Hoover says, " The subjecting of the oiled pulp to compressed air may be an essential part of the operation." It undoubtedly is, and this method is patented by Dudley H. Norris,[5] although opposed by Minerals Separation Ltd. when application for patent was made in England.

The De Bavay float is caused by air. Why is it not a froth?

[4] "Concentrating Ores by Flotation," by Theodore J. Hoover, Second Edition, page 117.

[5] U. S. Patent No. 864,856, Nov. 19, 1906.

the use of oil, which is not an essential element to flotation, as was shown above. Also these hypotheses assume that bubbles, existing as such in a liquid pulp, can then have mineral particles attached to them. If this be so, and it is not necessary to grow, as it were, the bubbles from the nascent gas in the liquid, why is it necessary to beat air into solution beyond the saturation point as is done in all froth-flotation machines using air as an adjunct except in the Callow machine? It would be much simpler to turn in a stream from a compressor or blower. If electrification is then all that is needed to produce attachment of the mineral particles, surely there are plenty of ways to electrify the bubbles. Thomas M. Bains [8] says, "It would seem easier, therefore, to electrify a bubble than to keep it from being electrified." No; something more than electrification is required of the bubble, as all who have tried to produce a float in this manner well know. James A. Block,[13] in his criticism on my article, says: "I cannot see how the water in a Callow or other pneumatic machine can become greatly super-saturated." This is best answered by Mr. Callow [9] himself: "The bubbles composing the froth are generated under a hydraulic pressure varying from 15 to 40 in." It matters not whether the water be saturated "with air at a pressure of several atmospheres," as was done by Norris, or under a hydraulic pressure of 15 inches, because, as I pointed out, it is not the air that is held dissolved, but it is the air that comes out, which is available for mineral attachment. A hypothesis based on nascent and occluded gas explains all kinds of flotation as well as all flotation machines.

More flotation experiments have been carried out in Australia than in any other country. No publication of systematic experiments to learn the reasons for flotation is so complete as that in the proceedings of the Royal Society of Victoria, by Kenneth A. Mickle.[10] His experiments (many of which I have verified in the laboratories of the Colorado School of Mines while experiment-

[8] "The Electrical Theory of Flotation," by Thomas M. Bains, Jr., *M. & S. P.*, Nov. 27, 1915, page 824.

[9] "Notes on Flotation," by J. M. Callow, *M. & S. P.*, Dec. 4, 1915, page 852.

[10] Vol. XXIII and XXIV (N. S.), Part 2, 1911. Abstracted in *Eng. & Min. Jour.*, page 307, Aug. 12, 1911 (Vol. 92), and page 71, July 13, 1912 (Vol. 94).

ing in the new testing plant there some three years ago with the Horwood process) showed nascent gas necessary and also that the particles must contain gas. He showed by experiments that (1) heat or reduction of pressure to liberate gas, that (2) generation of gas by means of acid, or that (3) super-saturation of solutions with gas, will cause minerals to float or tend to float without the aid of oil. He showed the effect of gases occluded by minerals to be (1) the particles are not wholly wetted when immersed in water; (2) the particles tend to float when sprinkled on water; (3) the particles when immersed collect bubbles as the solution is heated or exposed to vacuum and float or tend to float; and (4) the particles in gas-saturated solutions collect the bubbles evolved. He says, " In my earlier paper, it was shown that mineral particles absorb gases to an extent not previously suspected and that they retain the gas adsorptions with such persistency that they could neither be easily separated by mechanical means nor much affected by gravity and gas expansion." He also says, "In previous investigations, I found that carbon dioxide was obtained from all sulphides by aid of heat and exhaustion in the presence of water. It is probable that the gas-film can be expanded for removal in appreciable quantities only in the presence of water and that exhaustion in the dry state does not remove all the gas present."

With a view to further investigating the gas held by solids, he conducted the following experiments:

1. Copper and silver foil were cleaned with sodium hydrate and distilled water and dried. These and uncleaned pieces were treated in a vacuum-flask. Few bubbles formed on cleaned foil with distilled and air-free distilled water, but more on the uncleaned. All foil floated in tap-water.

2. Six steel needles were cleaned in the same way as the foil and allowed to stand one half-hour in alcohol and then dried in a desiccator. They would not float on distilled water until it had been exposed for some time to the air. Another set of needles and iron wire were similarly cleaned, but would not float until allowed to stand in a desiccator for two days. The same results were obtained with sulphides cleaned with sulphuric acid.

" These experiments show that perfectly cleaned needles and iron wire will float on the surface under the following conditions: (*a*) if the water is allowed to stand for some time in contact with air; (*b*) if the needles and wire are allowed to remain exposed to the air for sufficient time."

3. Cleaned and uncleaned pieces of iron wire, on being immersed in a saturated solution of carbon di-oxide, showed the following results: (*a*) clean pieces collected very few bubbles, while (*b*) unclean pieces were covered with a frost of bubbles.

I have confirmed these experiments, therefore I am positive of the incorrectness of Mr. Rickard's statement, " If you place an ordinary needle, say, a lace-needle suitable for use with No. 80 thread, on the surface of a bowl of water, it sinks at once to the bottom, in obedience to the law of gravity. If, however, you pass the needle through your hair, so that it becomes greased, it will float on the water." [11] This is the same old false assumption that oil is a necessity instead of an aid to flotation.

Swinburne and Rudorf [12] say, " A way of demonstrating the presence of gaseous envelopes is to sift some powdered substance which easily sinks, such as sand or ferrous sulphides, upon the surface of hot water, previously freed from gas by boiling. Bubbles of gas rise from the surface of solid particles." " It seems necessary that the gas should be produced at the surface of the particles themselves." " The air-film always plays an important part; and if the ore is thoroughly washed or boiled in water to remove the air-film, it cannot be concentrated with acid."

There are many other references all showing the same thing: that the mineral particles to be floated must contain gas so as to act as nuclei for the gas as it " comes into being " from the liquid. Therefore, in my former article, I did not present this evidence to prove my statement, which seemed a self-evident fact in view of the present knowledge of the subject.

[11] "What is Flotation?" by T. A. Rickard, *M. & S. P.*, Sept. 11, 1915, page 384.

[12] Paper read before the Faraday Society, Dec. 12, 1905, by J. Swinburne and G. Rudorf. Abstracted in *Eng. & Min. Jour.*, Feb. 10, 1906.

Mickle collected gases from concentrate made from Broken Hill material some of which contained:

(1)		(2)	
N	72%	N	82%
O	2	O	2
CO_2	26	CO_2	16

It is seen that these gases obey Henry's law, each existing independent of the others and not displacing the others as Mr. Block [13] says undoubtedly would be the case. An analysis of a sample from the Horwood process gave:

N	95%
O	1
CO_2	4

These three samples of gas became disengaged from three samples of concentrate which were allowed to stand. Afterward a vacuum applied to No. 1 sample (70 gm. sulphide) gave a further amount of 1.7 c.c. gas analyzing:

N	27%
O	14.1
CO_2	58.8

On raising the temperature to the boiling point and subjecting this sample to vacuum, there was then given off 8.9 c.c. of gas, which was found to be practically all carbon di-oxide.

From the No. 2 sample he obtained 18.5 c.c. gas of which practically all was CO_2. On subjecting minerals to reduced pressure and heat, he found that he could obtain more gas from calcite and quartz. This was mostly CO_2. He proved in all these cases that the CO_2 obtained was not from the decomposition of carbonates. This shows that minerals in general occlude gas, although Mr. Ralston [2] says that " good cases of occlusion have been found thus far only in amorphous substances." Mr. Block is quite right when he says " that it would be liberated with sufficient rapidity to float the particles does not seem probable." [13] Also Mr. Ralston [2] is correct in saying, " How the tightly-held gas could be liberated fast enough to compare with the exceed-

[13] James A. Block, *M. & S. P.*, Oct. 30, 1915, page 659.

ingly short time which it takes to accomplish flotation of a sulphide particle is difficult to explain physically." I simply stated that " if this gas be expelled from them, when they are in a liquid, at a time when the gas is expelled from the liquid, they become the nuclei for the formation of gas-bubbles." On the other hand, if bubbles are not formed from nascent gas of the liquid in contact with the mineral particle there can be no adhesion because the bubbles are surrounded by liquid films; or, if the particles contain no occluded gas, there can be no adhesion because the particles are surrounded by liquid films.

That these two words " nascent " and " occlusion " were objected to shows the necessity of extreme care in the choice of terms, and I am glad that Mr. Ralston brought up this point. " Nascent " is defined in Webster's New International Dictionary (3d), 1915, as follows: " Being born; coming into existence; beginning to grow; commencing, or in process of, development." The Century Dictionary, 5th edition, 1911, gives practically the same definition as follows: " Beginning to exist or to grow; commencing development; coming into being; incipient." The following usage is given: " Wiping away the nascent moisture from my brow: Barham, ' Ingoldsby Legends.' " Available gas of any kind for flotation must " come into being " in this way. Mr. Bains [14] excellently describes this, as follows: " If powdered galena ore, with a limestone gangue, be dropped into pure water, most of the powder will immediately sink to the bottom. As the air enclosed by the particles is expelled gradually, one sees the formation of ' armored ' bubbles, some of which may last for days. Here is flotation without oil or acid. If nitric acid be added, the gas-bubbles formed by the action of the acid on the gangue will carry up particles of galena." I have placed ½-inch pieces of quartz, galena, and other minerals in a beaker filled with water saturated with air at atmospheric pressure. The purpose was to watch the formation of the bubbles. More small bubbles formed on the metallic minerals when heat was applied. The bubbles formed on all minerals apparently in the

[14] "The Electrical Theory of Flotation," by Thomas M. Bains, *M. & S. P.*, Nov. 27, 1915, page 824.

same way that moisture forms on one's brow. I wish to describe this. There is only one single word in the English language that can be used to do it—"nascent." This is not "the dissolved gas that can be liberated," but it is the dissolved gas at the instant of liberation.

Regarding occlusion, Mr. Ralston has been kind enough to mention three ways by which gases can be held in solids, and I should have used more care in the choice of these terms. I used the word "occluded" as a general term to denote either surface adsorption or solid solution. As Mr. Ralston says, "this is a term the meaning of which has been much disputed." Trying to show that the gas in the mineral obeys the same laws as the gas in the liquid, as proved by Mickle, I spoke of the gas being dissolved in the solid and thus led up to the term "occlusion," having in mind the following: "The amount of gas which dissolves in a given quantity of water is proportional to the pressure, and from this experimental result, Van't Hoff showed mathematically by the principle of thermodynamics that, when in solution, this same gas must exert an osmotic pressure;" [15] and that "Substances dissolved by solids have an osmotic pressure as shown by Van't Hoff, so we can speak of solid solutions;" [16] also that "the greater the pressure to which the gas is subjected, the larger the quantity which will be adsorbed by the solid." [17]

Viscosity is another word that has been incorrectly used in connection with flotation. Mr. Rickard [11] in his article, "What Is Flotation?" states: "The combination of low tension and high viscosity enables a bubble of gas, rising through the liquid, to lift the surface film of the liquid, which the tension of the bubble-film is not strong enough to break, so the bubble endures;" and cites "A Text Book of the Principles of Physics," by Alfred Danniell, 1911. Also Mr. Rickard states: "Pure water has great surface-tension, it also has no superficial viscosity."

[15] "The Recent Development of Physical Science," by W. C. Dampier Whetham, page 113, 2d edition, 1904.

[16] *Zeit. Phys. Chem.*, 1890, 5, 322.

[17] "Elements of Physical Chemistry," by Harry C. Jones, 1902, page 267.

Viscosity as known today is an entirely different property of matter from that which Danniell in 1885 confused with surface-tension.

Perhaps the best definition of viscosity is by Harry C. Jones,[18] as follows: "We need simply mention here the works of Poisenille, Pagliani and Battelli, Slotte, Gartenmeister, and Traube" . . . "The monumental works of Thorpe & Rodger merit more careful attention." . . . "They prove conclusively, what has been hinted at before, that . . . viscosity may be taken as the sum of the attractive forces in play between the molecules; . . . It is, therefore, made evident that viscosity or inter-molecular attraction is in reality a property of the atoms of which the molecules are composed." This "superficial viscosity" is well explained in the *Encyclopædia Britannica*,[19] as follows: "The varying of contamination to which a water surface is subject are the causes of many curious phenomena. Among these is the 'superficial viscosity' of Plateau." . . . "Plateau attributes these differences to a special quality of the liquids named by him 'superficial viscosity.' It has been proved, however, that the question is one of contamination and that a water surface may be prepared so as to behave in the same manner as alcohol." Mr. Rickard, in his second article, page 517, *Mining and Scientific Press*, October 2, 1915, says: "To make bubbles, the surface-tension of water in the flotation-cell must be decreased by a contaminant and at the same time the viscosity of the liquid must be strengthened." As shown above, it is not the viscosity but the general surface-tension effect that must be strengthened. As I pointed out, a soluble or partly soluble oil will decrease the surface-tension of water because it dilutes the water, which has the greater surface-tension. By reason of this cause alone, the tendency to float is decreased and the bubbles burst more easily. Using a volatile oil in a M. S. machine, I have had the bubbles burst so violently that the cement floor was blackened with zinc sulphide at a distance of several feet from the machine. At the

[18] "Conductivity and Viscosity in Mixed Solvents," Carnegie Institute, Publication No. 80, 1907, page 19.

[19] 11th edition, under "Capillary Action."

same time I was making a very clean zinc concentrate from Leadville mixed sulphides after a Horwood roast. As no other contaminant was used, this was only made possible by having the mineral particles well oiled with the thinnest possible film to aid cohesion in armoring the bubbles well with the zinc-sulphide particles. In this case the surface-tension was still further reduced by the sulphuric-acid electrolyte.

Most oils, however, aid modern flotation in three ways, as I tried to point out in my former article, by (1) decreasing the force of adhesion of water for mineral particles by forming films around them, (2) increasing the cohesive force of the mineral particles for each other to aid in the formation of a network of mineral particles around the bubbles to toughen them, and (3) toughening the bubbles by forming films of oil around the bubbles in addition to those of the water. "Toughen" is not a good word whereby to express the meaning. Mr. Ralston explains this very well and at length on page 624, *Mining and Scientific Press* of October 23, 1915, under his interfacial tension hypothesis. He claims, however, "It is doubtful if the air-bubbles could be completely mantled by oil." This is contrary to the experience of others. "The colors on the bubbles indicate that they are mantled." This shows that Mr. Callow is right when he says "The bubble-mantles in a flotation machine are undoubtedly composed of oil, or oil emulsion." [20] The sum of these tension effects causes persistent bubbles, even though the surface-tension of the water has been reduced. These undoubtedly are extremely thin films, at least approaching one molecule in thickness.

Therefore molecular forces must be taken into account in dealing with them; as Mr. Ralston says, "The underlying cause of the tensions and of electric charges is the same thing—some strange molecular, atomic, or other force manifested in 'adhesion,' 'cohesion,' or even 'gravitation,' if you please." In dealing with these interfacial tensions, the drop-weight method cited by Mr. Coghill [21] for determining surface-tension is of no value to flotation.

[20] "Notes on Flotation," by J. M. Callow, *M. & S. P.*, Dec. 4, 1915, page 854.
[21] "Surface-Tension," by Will H. Coghill, *M. & S. P.*, Oct. 9, 1915, page 543.

The interfacial hypothesis of Mr. Ralston explains very well indeed the persistency of bubbles, but I am not so easily satisfied as is Mr. Block,[13] who says, " T. J. Hoover, for instance, in his book, ' Concentrating Ores by Flotation,' presents a consistent theory." Mr. Hoover (2d edition, page 72) says: " There has been no satisfactory theory yet propounded as to why acid does promote the preferential adhesion of water to gangue particles." Even the late electrical theory fails to answer all the questions asked by Mr. Hoover, on page 100 of his book. I answered the above question in my article by showing that an acid or any electrolyte creates osmotic pressure, by trying to enter the solid particles, of which their surfaces act as septums. If this pressure be sufficient to drive most of the gas out from the gangue particles, the metallic particles can be floated, for the reason that there is still left sufficient gas in them to become nuclei for bubble formation by the nascent gas of the liquid.

As shown by Mickle's experiments, mentioned above, there is more gas in sulphides than in other minerals and it is held more persistently in the sulphides. Thus a selective flotation is created. I have confirmed these tests.

Everyone who has experimented with flotation has seen how too much acid will " kill " the float. That is, the greater osmotic pressure drives the air from the metallic particles as well as from the gangue particles.

This effect is not to be confused with that caused by substances such as tannin or saponin mentioned by Mr. Callow [20] as colloidal impurities or volatile oils and the like, which destroy bubbles by reducing the surface-tension to the extent that the gas-pressure from within breaks or even explodes them. This weakening of the surface-tension by a colloid is an entirely different phenomenon from that shown when the osmotic pressure is increased by a crystalloid.

" The crystalloids when dissolved in water change in a marked degree its properties; for example, they diminish the vapor-pressure, lower the freezing-point, and reduce the boiling-point." [22]

[22] "Text Book of Physics," by J. H. Poynting and J. J. Thompson, 3d edition, 1905, page 186.

And as Dr. Lupke [23] states, the four laws in speaking of dilute solutions, are " Equimolecular solutions of any substances, prepared by using equal weights of the same solvent, exhibit equal osmotic pressure, equal relative depressions of vapor-pressure, equal risings of boiling-point, and equal lowerings of freezing-point."

In maintaining that osmotic pressure of an electrolyte is the cause of selective flotation, it is well to look into the motive power of osmosis. Kahlenberg [24] states it " lies in the specific attractions or affinities between the liquids used and also between the latter and the septum employed. These affinities have also at times been termed the potential energy of solution, etc.; they are, to my mind, essentially the same as what is termed ' chemical affinity.' " Or, as F. H. Garrison [25] put Taube's theory: " The driving force in osmosis is a superficial (or interfacial) pressure obtained by subtracting the surface-tension of one fluid from the tension of the fluid into which it diffuses." Or again as Van't Hoff and his followers contend " The molecules of a dissolved substance exert the same pressure against a semi-permeable membrane, during osmotic processes, as they would exert against the walls of an ordinary vessel were they in the gaseous state at the same temperature and the same concentration." [23] Since these authorities do not agree on the motive force of osmosis, investigation must rest for want of further data.

However, all theories of flotation, be they electrical or otherwise, must come to osmosis for their solution. This is not to question the fact shown by electrolysis that every atom of matter is capable of uniting with a definite quantity of electricity. Nor is it to question that corpuscles (later termed electrons by Dr. Stoney) do not revolve around atoms which are thousands of times larger. But it is to question any hypothesis that does not

[23] "The Elements of Electro-Chemistry," by Robert Lupke, 2d edition, 1903, page 119.

[24] *Jour. Phys. Chem.*, 1906, 10, page 208.

[25] " A Note on Taube's Theory of Osmosis and Attraction Pressure," by F. H. Garrison, Army Medical Museum, *Science*, Vol. 32, 1910, page 283.

take into account the fact that particles will not float when all the gas is driven from them. Osmotic pressure can free particles of their occluded gas. Whether osmosis is caused by electricity or whether a current of electricity is caused by osmosis has no bearing on flotation. However, in passing, it may be of interest to mention that Dr. Robert Lupke, in his book, " Elements of Electro-Chemistry " devotes Part III to " The Osmotic Theory of the Current of Galvanic Cells."

As mentioned above, extreme dilution of the electrolyte affects the osmotic pressure and selective flotation. With complete dissociation, as Arrhenius has shown, the ionized molecules are free to obey electric forces. It may be granted that air driven from a particle by osmosis may effect a change in the " contact-film " mentioned by Mr. Callow and leave the particle negatively charged, so that it would sink as described by him. Also it is granted that the mineral particles are all either negatively or positively (?) charged. Assuming the electric charges, there then enters the important question mentioned by Mr. Callow in stating his theory that " the particles possessing them will migrate when placed in an electric field." There is no question but that with an electric field, flotation can be produced in such a manner as described by Bothe Schwerin in his " Electro-Osmotic Process " [26] as follows: " My invention consists of adding electrolytes to the liquids containing the substances to be separated, the nature of the electrolyte depending upon the character of the substance. If the latter is of such a character that they would be deposited by the electric current on the cathode, electrolytes of acid character are employed; and if the substances would be deposited on the anode, electrolytes of basic character are used." Speaking of finely divided substances, sometimes indifferent to the action of an electric current, he continues: " I have found that such substances can be made electrically active by causing them to adsorb [here used as defined by Mr. Ralston] colloidal substances of a strong electro-positive or electro-negative character." Of the recent electrical theories advanced, none explains how this important electrical field, mentioned as necessary by

[26] U. S. Patent No. 993,888.

Mr. Callow, is created by any flotation machine. Mr. Block [27] shows this on a clay machine.

After selective flotation is created by osmosis, it matters not whether the particles be spoken of as being held together or to the bubbles by electric charges or by cohesion and adhesion in the way I mentioned. Sir Oliver Lodge,[28] after saying that "the force of chemical affinity has long been known to be electrical" goes on to say that "there is another kind of adhesion or cohesion of molecules, not chemical, but what is called molecular. This occurs between atoms not possessing ionic or extra charges, but each quite neutral, consisting of paired-off groups of electrons." However great this attraction may be, the mineral particles will not adhere to bubbles already formed, as was shown above; but, using them as nuclei, the nascent gas will form into bubbles to float them. Such gas formation is excellently described by Duhem [29] as follows: "From this, a bubble of vapor will never be formed in a region where the liquid is continuous; in fact, if such a bubble could begin to form, its radius would be at first infinitely small—less than the limiting radius of which we have spoken; whence, instead of continuing to grow, it would collapse." On the next page he continues: "These considerations do not apply merely to boiling; they completely explain a great number of phenomena."

The electrically-charged mineral particles may aid in bubble formation although they cannot effect attachment of mineral particles to bubbles already formed. Regarding this, Dr. Thompson [30] says that "the charged particles act as nuclei around which small drops of water condense, when the particles are surrounded by damp air cooled below the saturation point." "Experiments were made with air, hydrogen, and carbonic acid and it was found that the ions had the same charge in all the

[27] "Notes on Flotation." Discussion. Bulletin A. I. M. E., Dec., 1915, page 2337.

[28] Chapter 16, "Nature of Cohesion," in book "Electrons," by Sir Oliver Lodge, Principal of the University of Birmingham.

[29] "Thermodynamics and Chemistry," by P. Duhem, 1903, Art. 275, page 366.

[30] "The Atomic Structure of Electricity," Chapter 4, "Electricity and Matter," by J. J. Thompson. Lectures at Yale, May, 1903.

gases." Also, "Thus by suitably choosing the super-saturation, we can get the cloud deposited on the negative ions alone so that each drop in the cloud is negatively charged." Electricity may manifest itself in various ways, but flotation cannot take place without nascent or occluded gas.

THE THEORY OF FLOTATION[1]

By H. Hardy Smith

It appears to me that the problem of elucidating the theory of flotation could be greatly simplified by formulating some definite line of attack; the first consideration in which should be to segregate the various physical forces with their attendant phenomena, and to attack each in turn.

It is quite possible, in fact most probable, that some of the forces come into play in all the phenomena, but by delivering a massed attack on each section in turn, perhaps success can be achieved more easily.

I suggest the following as a possible segregation:

(1) The physical forces governing the formation of bubbles in a pulp.

(2) The physical forces governing the attachment of bubbles to sulphide particles in a pulp.

(3) The physical forces governing the stability of the bubble attachment.

(4) The physical forces governing the stability of a bubble at the free surface of the pulp.

Leaving out of consideration those processes in which bubbles are formed in a pulp by the chemical action of one substance on another, and also Mr. Norris's unique process, in which minute bubbles are "born" in a pulp which is super-saturated with a gas, and regarding only those processes in which a gas is introduced directly from an external source, segregation No. 1 will be found to present a considerable problem.

Several of your correspondents appear to be laboring under the delusion that it is simply necessary to introduce air violently

[1] From the *Mining and Scientific Press* of July 1, 1916.

into a pulp either by agitation or blowing, and immediately bubbles of the right number and kind obligingly form themselves. Anybody who has had practical experience with flotation, especially with the so-called air-froth flotation, knows that most unfortunately this is not the case. No amount of agitation or blowing will produce bubbles of the right kind and number in absolutely pure water. A contaminating agent is necessary, and as some of the contaminating agents commonly used happen to be oils, concentration by frothing most unhappily has been named "oil-flotation," thereby masking the real significance of the use of the reagent. The action of certain substances in producing innumerable minute bubbles when air is introduced forcibly into a pulp, seems to be of fundamental importance, since without these bubbles the most common forms of froth-flotation cannot be considered.

Professor Pollock of Sydney University, in Australia, has done some very interesting and useful work on this all-important subject, and I believe has formulated a theory. I once saw a set of instantaneous consecutive photographs of bubbles, taken by him, showing their formation after the introduction of a blast of air. With pure water the bubbles were mostly large, and even the small ones which were instantaneously produced had a tendency to collect together to form larger ones. With contaminated water the reverse was the case, the instantaneously produced large bubbles seeming to break down into smaller sizes.

From my experience in the practical application of the froth-flotation process, I am inclined to believe that many of the troubles that crop up from time to time at flotation plants are due to the inability of the reagent used to produce the required quantity of bubbles, owing to the presence of some reactive substance in the pulp. Hence practical, as well as theoretical, considerations demand a thorough understanding of the physical forces governing the production of bubbles in a pulp.

Coming now to segregation No. 2. More attention has been paid to this phase of the question perhaps than to any other, and rightly so, as it is of the utmost importance in all flotation processes, those employing the surface-film effect being excepted.

Many writers pass lightly over the problem and simply state that the bubbles attach themselves preferentially to the oil or gas-filmed sulphide particles.

Let us now see whether this is possible if the two forces of surface-tension and adhesion are alone considered. In the following discourse surface-tension can be most simply defined as that force acting at the surface of all liquids which continually tends to reduce the surface area; and adhesion as that force which acts across the interface between two substances, which are in infinitely close contact, and tends to keep them from separating.

Consider a particle of sulphide mineral (which, for the sake of clearness, we may assume to be nearly spherical) and a bubble in close contact, in the interior of a pulp, but before the bubble has actually " picked up " the mineral. (Fig. 1.) Even if the particle possesses appreciable adhesion for the water, the surface of the liquid in contact with the particle must be considered as tending to have surface-tension, although the tendency is opposed by the adhesion. (See T. J. Hoover's " Concentrating Ores by Flotation," pages 50 to 55.)

In the first case, assume the adhesion to be negligible. The surface-tension forces that now come into play are shown in Fig. 1, where Tg is the gas-liquid, and Ts is the solid-liquid surface-tension. A glance at the force diagram will show that whatever the value and direction of the forces Ts and Tg, their component Tc can never be greater than $Tg+Ts$. Therefore surface-tension alone cannot rupture the intervening film, and cause the bubble to envelop the particle. If the particle possesses appreciable adhesion for the liquid, then the case is more hopeless still, as Tc must then be sufficiently strong to rupture the intervening film and also to tear it away against the action of the adhesive force between the solid and the film.

Once a rupture has been effected, bubble attachment resolves itself into a struggle between surface-tension and adhesion, the former strongly favoring a strategical retirement to the rear, from the salient, so as to straighten the line, and adhesion endeavoring to hold the right wing to its position.

As it is an established fact (see Fig. 2) (Mr. C. T. Durell not-

withstanding) that a bubble contiguous to a surface with negligible adhesion does become attached almost immediately, so that its film forms part of a continuous film covering both solid

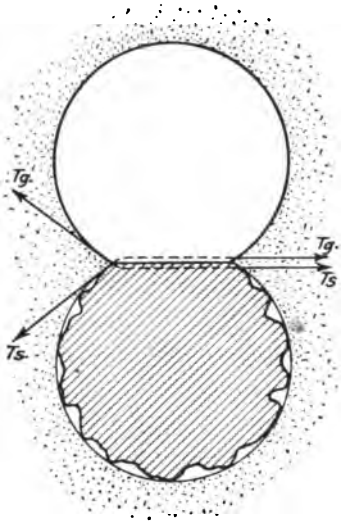
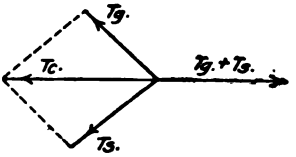
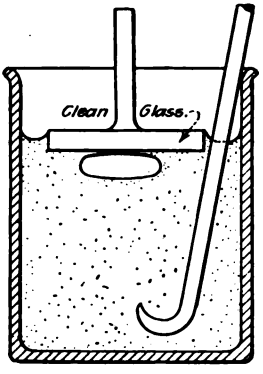


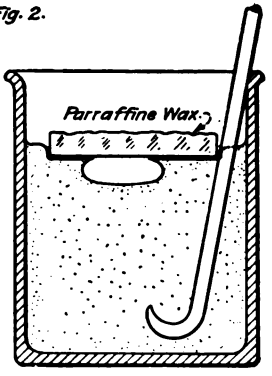
Fig. 1.





Bubble unattached
Bubble-Film continuous and
Bubble perfectly mobile.

Fig. 2.



Bubble attached and
Bubble-Film discontinuous.

and gas, there must be some force that causes rupture of the bubble-film at the point of contact.

In the case of two plain bubbles in pure water with their films in contact, the immediate coalescing can probably be explained by the difference in vapor-pressure existing in bubbles of different

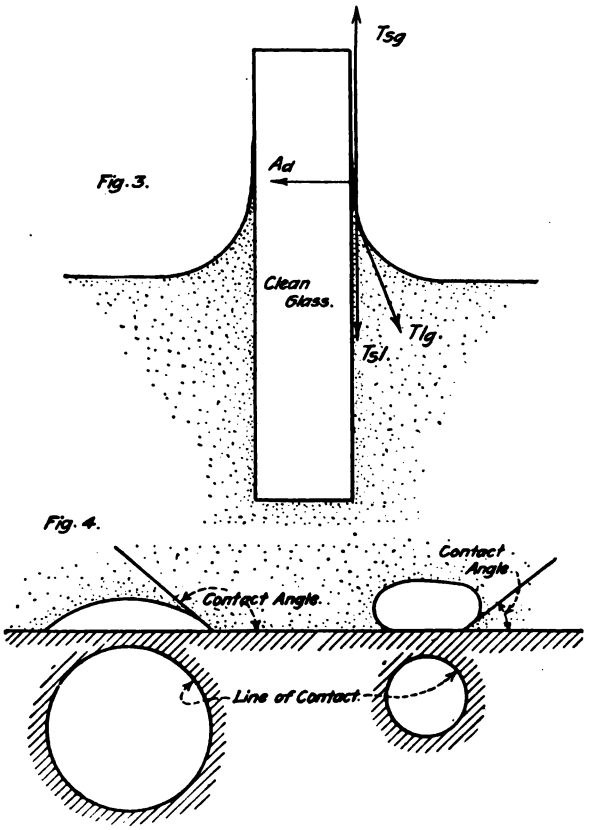
radii. But we add a contaminating agent for the very purpose of counteracting this force due to the difference in vapor-pressure so as to allow small bubbles to exist in the presence of larger ones; otherwise a froth would be an impossibility. Hence some force other than the difference in vapor-pressure must be present when one of the bubbles happens to have some, or all, of its interior space occupied by a sulphide particle.

In all probability this additional force manifests itself in the phenomenon known as the " hysteresis " of the contact-angle. Hysteresis is defined as the lagging of effect behind cause, and a contact-angle is the " effect " that is " caused " by bringing a solid surface in contact with a liquid surface in the presence of a gas. With many substances the " effect " (the contact-angle) does not assume its full value immediately, but lags behind. The reason why the angle changes can be fairly well explained if we assume that there is a force acting between a solid surface and a gas, tending to concentrate the gas on the solid surface; and that this force is strong enough to act across a thin film of the liquid.

In Fig. 3 the solid is a piece of glass, which is clean, and has been immersed for some time in the liquid. On drawing it through the surface, a contact-angle is immediately formed, and for any given angle, the forces *Tsg*, *Tlg*, and *Ad* are in equilibrium (ignoring gravity). If now the solid possesses the power to adsorb the gas through the very thin film at the toe of the angle, the adhesion of the liquid for the glass will be lessened and a corresponding surface-tension *Tsl* set up in the direction shown. This additional force will be sufficient to upset the state of equilibrium, the toe of the angle will recede, and the angle will increase in size. The stable angle will be reached when *Tsg*, *Tlg*, *Tsl*, and *Ad* have such magnitude and direction as to balance one another.

It has been found that those substances which possess the greatest power to vary the contact-angle also show the strongest tendency to float under suitable conditions, and it is reasonable therefore to assume that this power has something to do with the attachment of bubbles.

The problem presented by segregation (3) is not nearly so formidable as that just considered; it, as already stated, merely resolves itself into a struggle between surface-tension and adhesion. With most substances in their natural state, adhesion is altogether too strong, and, even if the film at the point of con-



tact is ruptured, the bubble cannot attach itself on account of the inability of the surface-tension to tear the solid and the liquid surfaces apart. Hence either the surface-tension must be increased or the adhesion decreased. The latter course is usually adopted, as with dilute solutions, the former is difficult; and except for very small amounts is an impossibility.

Although an absolute increase in the surface-tension is out of

the question, a relative increase is possible by raising the temperature. Both surface-tension and adhesion decrease with a rising temperature, but the latter much faster than the former; one being zero at the critical temperature and the other probably zero at the boiling-point. This is one of the reasons why solids that will not collect bubbles at ordinary temperatures will do so when the boiling-point is approached.

The usual methods employed for decreasing the natural adhesiveness of liquids for solids are:

(*a*) To allow the solid to take on a film of gas by adsorption (or occlusion?).

(*b*) To allow the solid to take on a film of oil or other greasy matter by adhesion.

(*c*) A combination of both (*a*) and (*b*).

While collecting evidence for one of the patent lawsuits that are ever with us, an interesting discovery was made. A piece of Broken Hill sulphide ore, taken from the centre of a large uncracked block, was found to contain 0.0037% of natural grease, as obtained by an ether extract. Samples were taken from several other mines, and all gave an oily residue after extracting with ether in a most careful manner. Perhaps it is just as well to add that this was discovered accidentally and was not being specially sought as prospective evidence. This discovery goes a long way toward explaining the preferential adhesion of bubbles to sulphide particles.

The tenacity with which the bubble holds the particle depends on the length of the line of contact, which in turn depends on the size of the contact-angle, itself proportional to the relative values of surface-tension and adhesion. (See Fig. 4.)

If the adhesion is negligible, and the particle is large in comparison with the bubble, the result would be as shown in Fig. 5-A.

If the particle is small, then the result would be as in Fig. 5-B.

As adhesion increases, the tendency is for the particle to get more and more out of the bubble and into the liquid until the surface-tension does not act over a sufficiently long line of contact to hold the weight of the particle, and it falls off.

The problem presented by segregation (4) has been dealt with in a most excellent manner by Mr. W. H. Coghill in the *Mining and Scientific Press* of February 26, 1916. His remarks in regard to a lowering of the surface-tension *per se* not being essential to the formation of a froth are most timely.

The tension that exists in a pure liquid film is unlike all other tensions with which we are familiar, in that the stress is not proportional to the strain. Within the elastic limit (that is, the limit wherein the substance will return to its original shape when the contorting force is removed) a steel rod, or, taking what is more familiar still, a steel spiral spring, needs twice the pulling force to stretch it twice as much, and so on. The well-known spring balance depends on this fact. But with a liquid

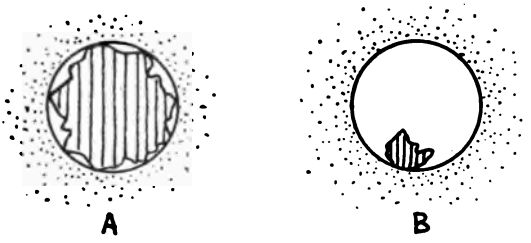


FIG. 5.

film the same force can continue to cause an extension until rupture takes place, in spite of the fact that the film, right up to the point of rupture, is within the elastic limit according to the above definition.

It is plain then that our common conception of a tension must be entirely revised when we come to deal with the tension at the surface of a liquid. For a system to be in a state of stable equilibrium it must offer a greater resistance to any force which tends to change its configuration, and as a pure liquid film does not fulfill this requirement it cannot possess stability.

The extreme instability of bubble-films is strikingly shown by the phenomenon in certain boiling liquids, with which we are all painfully familiar in our student days, called " bumping." In the absence of nuclei on which to form, the radius of a steam-

bubble when it first comes into being must be infinitely small, and the vapor-pressure to balance the surface-tension of these small bubbles is large. Therefore before the bubbles can expand and rise through the liquid (that is, before boiling can occur) the temperature must be raised above the natural boiling-point of the liquid. As soon as the bubble has expanded to appreciable size, the vapor-pressure of the liquid is in excess of that necessary to balance the surface-tension, and the bubble expands so rapidly that it literally explodes.

A boiler does not explode until its steel plates are actually ruptured, but the bubble explodes at the bottom of the beaker, that is, while its shell is actually in existence.

In the case of a solid, the greater the tension the greater the tensile stress developed; for a material of given strength, the greater the tensile stress, the greater the chance of rupture.

This line of reasoning does not hold in the case of a liquid film. The idea that a bubble-film can be ruptured by the force of its own surface-tension is about equivalent to the idea that a man can lift himself by his own shoe-strings.

It is obvious from the nature of the molecular forces engaged, that the greater the surface-tension the greater the ultimate tensile strength of the film. The lowering of the tension in itself therefore cannot give greater stability to a liquid film; but the surface adsorption, which accompanies the lowering of the tension in the case of certain solutes, can.

For reasons that need not be gone into, a solute which lowers the surface-tension of a liquid concentrates at the surface of the solution, but this process of concentration (called adsorption) takes a certain definite time to reach its full value. Now, if a film of the solution be stretched, new surface is produced, and this new surface at the moment of production possesses greater tension than the rest of the surface, because the surface adsorption has not had time to reach its full value. It therefore offers a greater resistance to the stretching force, and fulfills the conditions for stable equilibrium. So strong is the adsorption factor in certain cases, that practically the whole of the solute is concentrated in the surface layers, and therefore, although the abso-

lute quantity in the solution may be exceedingly slight, the surface effect it produces is considerable. This explains the efficacy of the extremely small amount of contaminating agent used in some froth-flotation plants.

In a mineral-froth, it is strikingly obvious that those bubbles which have their films thickly studded with sulphide particles have their stability enormously increased. In some froths, one such bubble can be seen pursuing the even tenor of its way, amid a regular holocaust of its less fortunate brethren. The reason for this is not quite clear, but it is probably due to the adhesive force between the liquid and the solid.

The above remarks are given for what they may be worth, in the hope that they may be of some assistance to other millmen, who, like myself, are anxious to see the inner workings of a flotation process clearly, as by the light of day, but at present, only perceive them dimly, as by the flicker of a candle at the far side of a 50-ft. stope.

THE FLOTATION OF MINERALS[1]

By Robert J. Anderson

Many phenomena are supposed to contribute to the flotation of minerals, whether in whole or in part is a mooted question. I shall only sketch roughly the present tendency of ideas and make no reference to the first early and crude notions, which are now mainly of historical interest.[2]

Surface-Tension has been well defined in articles appearing in the *Journal of the American Chemical Society* during the years from 1908 to 1913. The theory has been treated in particular by Laplace, Gaus, and more recently by Van der Waals, and by Willows and Hatschek.[3] As defined by Jones,[4] "potential energy, present at the surface of liquids, produces a tension which is known as surface-tension." The phenomena invariably indicative of surface-tension are: Drops of a liquid not exposed to an external force, that is, either suspended in another liquid of the same specific gravity or freely falling, assume a spherical shape, the sphere being that form of body with the smallest surface per given volume; further, if water be placed in an open vessel its surface film will be a measurable quantity, and its thickness will vary with a number of factors of which temperature is one. Its thickness is observed as ranging from 4×10^{-5} cm. to 4×10^{-8} cm., and its density, when referred to the main bulk of the water below, will approximate 2.14. Surface-tension is not affected by the surface area. It is numerical in value and expressed in dynes per centimetre. It is a variable factor dependent on tem-

[1] From the *Mining and Scientific Press* of July 8, 1916.

[2] Abstract of paper read at the Arizona (September, 1916) meeting of the American Institute of Mining Engineers.

[3] Willows and Hatschek: "Surface Tension and Surface Energy," 1915.

[4] Jones: "Elements of Physical Chemistry," 1907.

perature, increasing numerically with falling temperature, for example, water at 18° C. has a surface-tension of 73 dynes per centimetre, and at 0° C. this increases to 75 dynes. At the critical temperature of a liquid its surface-tension becomes *nil*.

All liquids have a definite cohesion or tensile strength, which is ascribed to the mutual attraction of their molecules. This then is comparable to a pressure existing within a liquid, which has been termed the " intrinsic " pressure. Naturally the value of the surface-tension of solids is numerically high. The surface-tension of a pure liquid against its vapor is markedly affected by the addition of soluble contaminants. Some salts will raise the surface-tension of water while others will lower it; the fact that the salts of weak acids will lower the surface-tension of water is explained by the fact that free acid is liberated by hydrolysis. It is further known that all acids will lower the surface-tension of water, which is also decreased by the addition of oil, or, in other words, oil will reduce the interfacial tension between the water-air phases. A phenomenon for which no explanation has been given is the one showing that the addition of contaminants may either raise or lower the surface-tension of water, but such addition, while it may decrease that tension greatly, can increase it only slightly. Any lowering of surface-tension is more marked in a liquid that has a high surface-tension, such as water, than in liquids of low surface-tension.

There can be, of course, no surface-tension without adsorption, which produces, in the case of positive adsorption, an increased surface concentration resulting from a lowering of the surface-tension by the contaminating and dissolved substance, whatever it may be. The equation of Gibbs ($u = -c/Rt.do/dc$) gives the relationship between surface-tension and the distribution of the solute between the bulk of the liquid and the film interface. Here the notation is:

u = excess of substance in the surface layer;
c = concentration in the main body of the liquid;
R = the gas constant;
t = absolute temperature;
o = surface-tension.

This shows that when the surface-tension is reduced by the addition of a contaminant, the quantity do/dc is negative and u is positive (from algebraic consideration). The surface film then contains more of the contaminant than the main body of the solution. If the surface film contains less of the contaminant than the main body of the solution it is a case of negative adsorption.

As given in the foregoing, the surface of a liquid against its vapor is in tension; the surface of liquid against another liquid, or a gas or solid, is also in a state of tension, termed interfacial tension. In the flotation machine the following conditions obtain: Pulp consisting of ore of approximately 80-mesh, water in ratio of 3 : 1 of ore, and oil in disappearingly small amount, is being violently agitated. For the sake of a specific case, the air is being forced mechanically into the swirling pulp by beaters or stirrers. The phases present in flotation by the oil-froth process are therefore: solid-liquid (ore-water), solid-liquid (ore-oil) solid-gas (ore-air), liquid-liquid (water-oil), liquid-gas (water-air), and liquid-gas (oil-air). Thus six tensions are present, but if the oil is soluble in the water the tensions are reduced to three. It is known that pure water cannot be made to maintain a persistent froth because its surface-tension is too high. Acid, if present, will lower the surface-tension of water, as will oil, if it is soluble.

Certain metallic sulphides, such as galena, have the power of floating on undisturbed water; they are not wetted and the curve of contact is convex. Some gangue minerals, such as quartz, possess an adhesive force of attraction for water that exceeds the intrinsic pressure of the water: they are therefore wetted and sink to the bottom, being drawn through the surface film. Such properties of the minerals are affected by the presence of oil, acid, and other reagents. Oil has a greater adhesive attraction for sulphide minerals than for gangue minerals; and the addition of acid and oil (if it is soluble) acts as a contaminant that will lower the surface-tension of the water and aid in the production of a persistent froth. Let us now look into the question of adsorption and see what part it plays in flotation, since it is so requisite to the production of a variable surface-tension.

Adsorption.—Generally speaking, adsorption deals with the unequal distribution of substances at the interface between dissimilar phases such as, solid-solid, solid-liquid, solid-gas, liquid-liquid, liquid-gas, and gas-gas. It is purely a physical effect. Commonly, adsorption [5] is construed to be the result of the condensation of a disperse phase upon the interfacial boundary solid-liquid. Returning for a moment to the Gibbs equation quoted above, adsorption may occur if the interfacial tension solid-liquid is reduced, this being positive adsorption. If, however, such an interfacial tension is raised in value it is a case of negative adsorption, as the solute or disperse phase will be rejected from the surface. Any condensation, strictly stated, of a solute or disperse phase in the interfacial boundary separating liquid-liquid or liquid-vapor is held to be a special case of adsorption. However, in the general sense, the phenomenon is looked upon as being the result of condensation of a disperse phase in the interface of two immiscible phases. Adsorption is shown strikingly by colloid gels—the product obtained by the coagulation of sols—and certain cases of selective adsorption are most remarkable. Adsorption will naturally vary with the surface exposed. In Miss Benson's experiments with amyl alcohol in aqueous solution, amyl alcohol reduced the surface-tension of the water, and it was found by producing a voluminous froth that the alcoholic concentration in the froth exceeded that in the bulk of the aqueous solution by about 5%. A froth has a very large surface, and it would be expected that the adsorption would be greater. Such experiments prove the value, qualitatively, of the Gibbs rule.

Recent work shows that all solids do condense gases on their surfaces and retain them there with great tenacity. Liquids in like manner adsorb gases. Further, liquids and solids exhibit selective adsorption of gases. Although this selective adsorption obtains, no proof has been submitted indicating that the amount of gas adsorbed by one substance is largely different from the amount adsorbed by another substance. An electric charge on an adsorbed substance probably would influence the amount

[5] Briggs: *Jour. Phys. Chem.*, Vol. XIX, No. 3, p. 210 (March, 1915).

adsorbed. The adsorption of air plays an important rôle in flotation, for, as Breuer points out, the adsorbed air-film is enormously responsible in preventing the coalescence of solid particles.

A comprehensive study of the adhesion of small particles of solid to the dineric interface (surface separating two liquid phases) has been made by Hofmann [6] based on the theory of Des Coudres.[7] From the standpoint of flotation this may be given as follows: If a solid particle, such as quartz, is wetted much more strongly by water than by another liquid, such as oil, the water will displace the oil, and a film of water will form about the quartz particle according to the relative forces of adhesion. Then the quartz particles will remain in the water phase if the water has a specific gravity greater than the oil, regardless of their size; but if now the oil has a greater specific gravity than the water, then the quartz particles will remain in the water phase until the size of the particles is such that the force of gravity will remove them from the water. Conversely, if a solid particle, such as galena, is wetted more strongly by oil than by water, the oil will form a surface film about the particle and hence prohibit the particle from being wetted by water, that is, from entering the water phase. Then the galena will only enter the water phase when the water is more dense than the oil, and, further, when the galena particles are such a size that the force of gravity overcomes the adhesion of the oil film to the oil.

Returning to purely theoretical considerations, Hofmann draws certain conclusions that deal with the supposition that solid particles will then remain in the surface separating two immiscible liquids, if those particles are wetted partly by each liquid. I quote Bancroft at length on this matter.[8] " The solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid; they tend to go into the other liquid phase if they tend to adsorb the other liquid to the practical exclusion of the water; while the particles tend to go into the dineric interface in case the adsorption of the two liquids is suffi-

[6] *Zeit. Phys. Chem.*, Vol. LXXXIII, p. 385, 1913.

[7] *Arch. Entwicklungsmechanik*, Vol. VII, p. 325, 1898.

[8] Bancroft: *Jour. Phys. Chem.*, Vol. XIX, No. 4, p. 287 (April, 1915).

ciently intense to increase the miscibility of the two liquids very considerably at the surface between solid and liquid."

Any simultaneous adsorption of two immiscible liquids by a solid would tend to form a homogeneous liquid phase at the surface of the solid.

In regard to the effect of contaminants or other impurities in contact with two immiscible liquids, this condition obtains: If the contaminant is soluble in one liquid but not in the other, and also lowers the interfacial tension of the two, the equation set forth by Gibbs exacts the requirement that the contaminant should obtain in the interface. Examples of this prove the validity of the law.

The terms adsorption and absorption have been used interchangeably in some writings, thus contributing to the already existing confusion of ideas.

Absorption or Occlusion.—There are three ways by which gases can be held with reference to solids: (1) By surface adsorption; (2) in solid solution; and, (3) by occlusion. The term " occlusion " has been applied indiscriminately to any of these methods by which gases are held by solids. Strictly speaking, by " occluded " gas is meant gas that is absorbed and held in finely-divided pores or openings, which may be of microscopic size. A recent theory [9] holds that occlusion plays the operative rôle in the flotation of minerals by all processes. I am unable to reconcile myself to this explanation, for a number of reasons. Marked instances of occlusion at normal temperature are known only in certain amorphous substances, like charcoal. Many metals, of course, both in the liquid and solid states, have the power of occluding gases, often in marked degree. There may be and undoubtedly are fine pores in the floatable minerals, which may in a sense be considered as an assemblage of capillary tubes; these can and do occlude gas. Yet occlusion is marked only in amorphous substances and in certain metals as just stated. It is definitely known that occluded gases are retained with great tenacity by the substances occluding them and therefore are

[9] Durell: *M. & S. P.*, Vol. CXI, No. 12, p. 428 (Sept. 18, 1915) and Durell: *Met. & Chem. Eng.*, Vol. XIV, No. 5, p. 251 (March 1, 1916).

expelled only with difficulty. It seems anomalous to hold that the occluded gas can depart from the mineral occluding it with sufficient speed to aid the air-bubbles in the liquid in the process of flotation. I believe firmly that occlusion is not a cogent factor in flotation, and that a more consistent theory may be formulated without postulating these conjectures regarding occlusion.

Colloids, in the original definition of the term by Thomas Graham, do not constitute a definite class of substances; a large number of different substances may be made to assume the colloidal state if proper precautions are taken. All of which reveals the striking fact that this colloidal condition is a *state* and not a *form* of matter. The ultra-microscope of R. Zsigmondy and H. Siedentopf has greatly increased our knowledge of colloids. A general statement may be made regarding colloids: that they do not show osmotic pressure in appreciable amount. Colloidal solutions—sols—are regarded as systems of two phases, in which the dissolved substance is the disperse phase and the solvent the continuous phase.

Since, in flotation, the ore is often as small in size as certain of the colloids, the pulp (ore, water, etc.) can be looked upon as a coarse suspension, and the laws of colloids apply here with equal force as in the realm of colloidal chemistry. So-called suspensions are systems consisting of solid particles of microscopic size distributed through a liquid. As mentioned by Ralston,[10] Reinders has treated at length the particular case of a solid phase maintained in contact with two liquid phases, that is, two immiscible liquids. His work is based on the different interfacial tensions existing, and his experiments and those of Hofmann, as mentioned in an earlier paragraph, have considerable bearing on the flotation problem.

Emulsions are fairly coarse dispersions of one liquid in another with which it is immiscible. The simplest and commonest emulsions are the pure-oil water emulsions, containing no emulsifying agent such as soap, proteids, etc. In such systems the oil globules can be coagulated by electrolytes, they show the Brown-

[10] Ralston: *M. & S. P.*, Vol. CXI, No. 17, p. 623 (Oct. 23, 1915).

ian movement strikingly, and can even be retained by some filtering media. Any process of emulsification is dependent on a lowering of surface-tension, or, to be more precise, on a lowering of the interfacial tension between the two phases. According to Briggs and Schmidt [11] the two essential requirements of an emulsifying agent are: (1) The property of condensing by adsorption in the dineric interface; and (2) the ability to form under these circumstances a strong coherent film. Temperature is a decisive factor in emulsification, for its effect is to reduce the interfacial tension between phases and also to lower the viscosity of the phases. In the production of emulsions, a considerable amount of surface energy is produced because of the relatively large surface area of the disperse phase; an emulsion is the more speedily effected if such surface energy be reduced by the use of a liquid having a low surface-tension as the continuous phase. Some emulsions, under certain conditions, display a great increase in viscosity over that of either of the immiscible phases, for example, the emulsions of the Pickering order—up to 99% of oil in 1% of soap solution—can be cut into cubes. Any emulsion produced with soap solution is at once destroyed by the addition of acid, as the latter will decompose the soap.

If solid particles are suspended in a liquid, they tend to increase the viscosity of that liquid gradually, depending on the amount of solid particles present. Experiments have shown that whenever a substance in suspension is wetted by two immiscible liquids simultaneously, it will go into the dineric interface in the manner already mentioned, and will tend therefore to produce an emulsion. If, however, the suspended particles cannot coalesce, owing to adsorbed oil film or for other reasons, and thus effect the production of a coherent film, the emulsion will not be stable. Few data are available on the production of emulsions by the oils used in flotation work, or on the matter of interfacial tensions between such oils and water. However, we are no doubt dealing with emulsified or partly emulsified pulp in some of the flotation processes, in the oil-froth process at least.

[11] Briggs and Schmidt: *Jour. Phys. Chem.*, Vol. XIX, No. 6, p. 479 (June, 1915).

Electrolytic and Electro-static Phenomena.—Any substance placed in contact with water or many other liquids will assume an electric charge, the origin of which is, as yet, not set forth. Most substances when in contact with water become negatively charged, but these charges can be differed at will or reversed by the addition of the proper electrolyte in requisite amount. These electric charges are by no means confined to sub-microscopic particles, but are found also on the particles of a coarse suspension. Gangue minerals, such as quartz, when suspended in water, are negatively charged, and sulphide minerals, such as pyrite, are positively charged under like conditions. Oil drops are negatively charged, as are air-bubbles under certain conditions. These charges are very minute when referred to the mass of the particle. Substantial evidence is at hand to show that floatable minerals have the positive sign of electricity when suspended in water or can be made to assume that sign by the addition of proper electrolytes in sufficient amount. As Callow [12] observes, there is a parallelism between electro-static characteristics and the flotative properties of ores. Many of the electro-static principles have either been carried too far or misapplied, as recent work shows.

Experiments in colloid chemistry indicate that the contact-films are charged and that such charges affect the dispersion or coherence of the particles in suspension. Of course, oppositely charged contact-films will coalesce while similarly charged contact-films will repel each other, if the charges are sufficient in amount to overcome the force of cohesiveness; in the latter, dispersion is the result. The oil and air contact-films having negative charges would tend to attract the sulphide particles, but further than this possibility electro-statics probably plays little part in flotation.

It is admitted that only minerals that are good conductors are suitable to flotation. As the electrical theory contends, electrified bubbles must be supplied to float the conducting minerals that are attracted, leaving behind those that are not. The bubbles in flotation are simply air spaces contained by a mantle of

[12] J. M. Callow: Bulletin A. I. M. E., No. 108, p. 3342 (December, 1915).

oil or of water, and there is, therefore, nothing within to bear the charge. In case it could carry a charge, which would only be possible by the presence of contained ionized gases or water-vapor, the charge would be speedily dissipated by contact with the interfacial boundary. Then in order that a bubble may carry a charge it must be protected by a dielectric film. Further, electro-statics plays probably little part in holding the sulphide particles and the gas-bubbles together, as neither the bubble nor the particle can have a charge of sufficient magnitude when referred to the size. The electrical theory has been strongly championed by at least one writer [13] and has been tolerated by some others. A recent article [14] indicates that the principles of electro-statics have been considerably misapplied. It is my belief that electro-statics may be a small contributing factor in flotation in a manner not as yet understood because of a lack of information concerning charges at the interfacial boundary between immiscible phases, for example, where the colloidal state is introduced in oil-water emulsions. Apparently, the electric theory is not important.

Froth and Bubbles.—The idea has been abandoned by most people that a low surface-tension is the essential requirement for froth formation. As mentioned by Coghill in a recent writing,[15] the contamination of the liquid with an impurity that will cause a variable surface-tension is the real requirement. A bubble of air is spherical in shape and this shape can only be maintained if the external pressure exceeds the internal pressure. Since a bubble does not expand *per se*, large bubbles can only be accounted for by heat, coalescence, or electrification. Viscosity is an important factor in froth-persistence, as it increases the tenacity of the liquid film and thus prevents ready rupture. The rupture or bursting of bubbles is explained thus:

[13] Bains: "The Electrical Theory of Flotation," *M. & S. P.*, Vol. CXI, No. 22, p. 824 (Nov. 27, 1915) and Bains: "The Electrical Theory of Flotation," II, *ibid.*, Vol. CXI, No. 24, p. 883 (Dec. 11, 1915).

[14] Fahrenwald: "The Electro-statics of Flotation," *ibid.*, Vol. CXI, No. 11, p. 375 (March 11, 1916).

[15] "The Science of a Froth," *M. & S. P.*, February 26, 1916.

1. Concussion upon a surface film deficient in the requisite viscosity and variable surface-tension.

2. Relief of pressure—here the gas of the bubble in expanding exerts a pressure exceeding that of the liquid film.

3. Adhesive force of the entrained gas for the atmospheric air.

4. Evaporation of the liquid film.

Flotation bubbles will burst for any one or a combination of these reasons.

Solutions in which the continuous phase is a solution of soap, various products from the saponification of albumens, etc., will froth voluminously even in a very diluted condition; frothing never occurs in pure liquids and is a definite proof that the solute or disperse phase lowers the surface-tension of the solvent. A froth, which shows adsorption at the interfacial boundary of solution and gas, depends for its persistence on the production of a viscous film at that boundary; these viscous films are the direct result of surface adsorption of the disperse phase, that is, dissolved contaminants, the amount of which is small—disappearingly so. The work of Hall and of Miss Benson shows that in a foaming liquid the foam is richer in the dissolved contaminant than is the bulk of the liquid. Froth formation in the Callow cell is the result of the injection of air into the pulp (already emulsified); the froth persists as long as there is sufficient air injected into pulp of the proper consistence. The froth in the Callow cell is governed in nature by the kind of oil used and by the amount of air. A pneumatic froth is unstable or ephemeral; it dies rapidly when removed from the influence of the injected air. The mechanical froth, on the other hand, is thick and persistent, and must be broken up in de-watering the concentrates.

Oils have a selective action for metallic sulphides, tellurides, and some other minerals. The fact that both the oil and the air or other gas have a selective adhesion for sulphides prevents them from being wetted by water. Conversely, the quartz and other minerals exhibit just the opposite characteristics. The gangue-minerals, generally, do not exhibit adhesion for either

The main and essential requirements for froth-flotation are: (1) the production of a persistent froth; (2) the attachment of the bubbles of air to the sulphides or other material to be floated; and (3) the maintaining of a selective action by the froth bubbles for the sulphides or other material to be floated.

PRINCIPLES UNDERLYING FLOTATION[1]

By Joel H. Hildebrand

Introduction.[2]—The phenomena involved in ore flotation are mostly effects of surface-tension, so that an understanding of this force and how it may be modified by various factors is fundamental to a scientific study of flotation.

Wherever different phases are in contact we have surfaces where the effects of surface-tension may be apparent. It will be convenient, for our purposes, to classify the boundaries between phases as follows: (1) liquid-gas, (2) liquid-liquid, (3) liquid-solid. The boundaries solid-gas and solid-solid will not be considered, being unimportant from the standpoint of our subject. Since the effects of surface-tension are increased as the surface between the phases increases in extent, we will be led to consider the systems encountered in flotation processes, in which one of the phases is highly dispersed. These systems, corresponding to the above classifications are (1) foams, in which the gas is highly dispersed in the liquid (the other system, fog, in which the liquid is dispersed in the gas does not here concern us); (2) emulsions; (3) suspensions.

Liquid-Gas Boundary.—(*a*) *Definition and Measurement of Surface-Tension.*—It is found that all liquids have a tendency to assume a form which will have the smallest surface. Where the liquid is supported by a surface that it does not wet it tends, for example, to assume a spherical form, manifest especially with small drops, where the influence of gravity is small. A soap-bubble tends to contract, expelling the air through the orifice of

[1] From the *Mining and Scientific Press* of July 29, 1916.

[2] Abstract of an illustrated lecture delivered before a joint meeting of the San Francisco section of the American Institute of Mining Engineers and the California section of the American Chemical Society, February 15, 1916.

the pipe from which it is blown. A liquid that wets the walls of a tube will be drawn up into it. The magnitude of this force can be measured by various methods, such as the rise in a capillary tube, the shape of a drop under the opposing action of surface-tension and gravity, the weight of a drop that surface-tension will support as a liquid issues slowly from a tip of definite size. A general idea of the magnitude of this force may be obtained from the values given in Table I.

TABLE I

Liquid.	Temperature, ° C.	Surface-Tension, Dynes per Cm.
Hydrogen	−252	2
Carbon disulphide	20	33.5
Alcohol	20	22
Water	20	73
Ether	20	16.5
Mercury	18	436
Gold	1070	612
Sodium sulphate	880	187

(*b*) *Cause of Surface-Tension.*—It must be noted that we can define and measure surface-tension without making any assumptions whatever as to what causes it. The fact that the surface tends to contract with a definite force does not mean that the surface is coated with anything like a rubber membrane. The surface of a liquid, except for a slight difference in density, is doubtless the same as the rest of the liquid. The existence of surface-tension is to be attributed to inter-molecular attraction. Consider a molecule, such as *a* in Fig. 1, in the interior of a liquid. It will be attracted by the surrounding molecules, and these attractions may be resolved axially into four equal components, as shown in the figure. Consequently nothing but viscous resistance would oppose the moving of this molecule to another portion of the liquid, provided it remains in the interior. The moment, however, it approaches sufficiently near the surface, the upward component of molecular attraction is reduced, becoming zero at the surface at *b*, if we neglect any effect of gas or

vapor above the surface. The result is that we have to do work upon each molecule brought from the interior to the surface of a liquid, and any considerable extension of its surface involves the doing of a considerable amount of work against a force the component of which along the surface of the liquid we call " surface-tension."

(*c*) *Effect of Temperature.*—Since the increase in kinetic energy of the molecules with temperature forces them farther apart we should expect inter-molecular attraction and hence surface-tension to diminish with increasing temperature, and such is indeed the case. At the critical temperature, where the density of the vapor becomes the same as that of the liquid, the surface-tension becomes zero, of course.

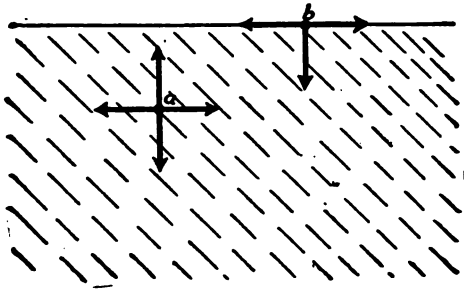


FIG. 1.

(*d*) *Effect of Dissolved Substances.*—The surface-tension of mixtures of liquids is usually less than that which would be calculated on an additive basis, so that the more general tendency is for solutes to lower the surface-tension of the solvent. We find that the surface-tension of water is usually raised by dissolved salts, and lowered by other liquids, and especially by organic colloids, such as albumen, glue, soap, saponin, etc. Moreover, it is possible to show thermo-dynamically that solutes which lower the surface-tension of the solvent tend to concentrate at the surface, still further lowering the surface-tension there. For this reason very different figures are obtained for static and dynamic measurements of surface-tension with solutions of such substances. Table II shows the results of such measurements with sodium oleate (soap) solutions.

water, where the surface-tension of the water is much lowered as it is in meat-broth by the presence of albumin, gelatin, etc., the value of a is small enough to allow any oil present to remain as lens-shaped drops.

(*b*) *The Stability of Emulsions.*—This is obviously favored by a low surface-tension between the phases, by viscosity, by the presence of a substance tending to form a skin preventing the droplets of the enclosed phase from coalescing, as they naturally tend to do, and most important of all, the presence in the phase that is to enclose the other of a substance that will be positively adsorbed at its surface, thus making stable a film of the liquid separating two droplets of the other, enclosed, liquid. The enclosed phase takes the place of the bubbles in the previous discussion of foam stability. By a suitable choice of solutes either

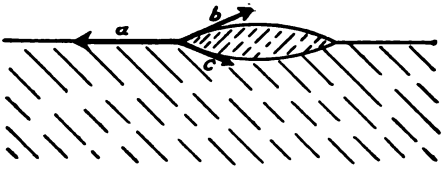


FIG. 3.

phase may be made the enclosed phase. For example, when soap is added to water the films of water become stable, and a liquid like benzene may be made to form a stable emulsion in water. On the other hand, when a magnesium soap is dissolved in benzene, films of benzene become stable, and benzene will yield both stable foams and stable emulsions with water as an enclosed phase.

Liquid-Solid Boundary.—With a boundary of this sort direct measurement of surface-tension is impossible, but relative values may be inferred by noting the wetting power of a liquid for a solid, especially as indicated by the angle of contact. When, for example, a drop of water is placed upon a bright metal surface, instead of spreading over the surface of the latter as would kerosene, it remains in drop form, its surface meeting the metallic surface at a certain angle. When a drop of castor-oil is placed

on the metal it forms a much flatter drop, the angle being different, corresponding to greater wetting power for the metal. The surface-tension between these phases can be altered as before by the addition of adsorbed solutes, so that a drop of soap solution will be much flatter when placed upon the metal than the drop of pure water. This wetting power is also different for the same liquid upon different solids, as is illustrated by the experiment shown in Fig. 4, where the angles of contact indicate that when chloroform and water are in competition the former has greater wetting power for a metal surface, while the latter has greater wetting power for glass. It would seem that determinations of these angles should offer a valuable preliminary to flotation experiments.

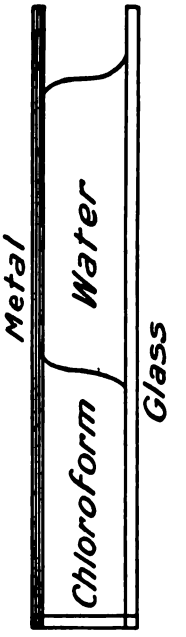


FIG. 4.

As a consequence of this relative wetting power, if a layer of kerosene is placed over water, and a powdered silicious material dropped into the vessel, it will stop only momentarily at the oil-water surface. As fast as the oil can be displaced by the water the particles drop through into the water phase. If, however, a metallic powder, or a sulphide with metallic lustre, be dropped into the vessel, it remains in the oil phase, supported, if the mass is not too great, by the surface-tension at the boundary.

The ease with which a solid particle can float on the surface of a lighter liquid depends upon its size, the difference in density of solid and liquid, and the angle of contact the liquid makes with the solid. The relationship is expressed in Fig. 5, where we assume, for simplicity, a cylindrical particle of radius r, height h, and density d, floating on a liquid of density d_2 and surface-tension s. The maximum effect that could be exerted by gravity upon the particle would obviously be $\pi r^2 hg(d_1 - d_2)$ dynes. If the solid were not wet at all by the liquid and the angle of contact were zero, the upward force tending to prevent the particle from sinking into the liquid would be $2\pi rs$. In an actual case,

however, where this angle is a, the upward force is $2\pi rs \cos a$. It is obvious that the floating tendency would be greater the smaller the particle, the less its density relative to that of the liquid, the greater the surface-tension of the liquid, and the smaller a. In floating-practice the densities are not to be altered, the size of the particles is made as small as is consistent with economical grinding and subsequent recovery, the surface-tension of the water cannot be increased, but is rather decreased by the agent added to produce foaming. The foaming gives a large surface, as the total quantity of ore floated is proporti..al to the surface

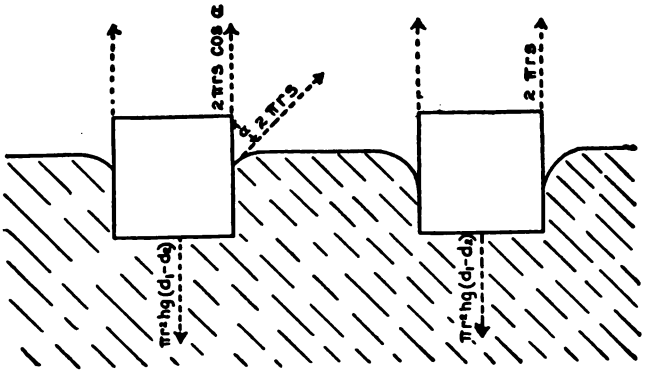


FIG. 5.

of the water and not to its volume. The most effective modification that can be made in the above factors is to decrease the angle a as much as possible for the ore particles, while still leaving it greater than 90° for the gangue particles, the condition necessary that the latter should sink. This is the purpose of the small quantity of oil added during the grinding of the ore. The wetting power of oil for a metallic surface causes the oil, if the right kind, to spread over the metallic surface as it would over the surface of water. The water present at the same time wets the gangue preferentially, preparing for the separation that results when the large amount of water is added. It is obvious that the frothing-agent necessarily added later works against the effect here desired of the least possible wetting of the ore, as it

decreases the surface-tension both at the liquid-air and at the liquid-solid surfaces.

A word might be said in conclusion about the stability of suspensions. Besides the stabilizing influences important in the case of foams and emulsions, another here rises to great importance, namely, the electric charges on the suspended particles due to adsorbed ions. This effect may be illustrated by dividing a suspension of fine silica into two portions, and adding to one a little acid and to the other a little alkali. It is found that in the second case the suspension is quickly flocculated and settles out, while in the acid solution it remains suspended for a long time. Reference must be made to works upon colloids for further discussion of the many interesting phenomena connected with such behaviors. In ore flotation, the effect of even slight amounts of acid or alkali may be, aside from that just mentioned, to clean the ore particles and thus expose a more truly metallic surface to the oil, and to affect the surface-tensions involved, especially by modifying chemically the other substances added, notably the frothing-agent.

MOLECULAR FORCES AND FLOTATION[1]

By Will H. Coghill

The warning about young men specializing in flotation, as sounded by E. P. Mathewson in a recent number of the *Mining and Scientific Press*, should be considered by all who are directing these men in their education. It provokes the question that ever confronts the instructor in a technical school.

The student may be drilled on the design and construction of the various flotation machines, and the methods and results of the experimenters, and be sent into the field feeling that he is strictly up-to-date, but his school-work would not amount to much if he has been taught only the ever-changing art. He would have acquired something more enduring and be better prepared to benefit from his college course had he been taught natural laws with enough of the art to give a view of the field to which the laws could be applied, for man's methods are ever changing while Nature's laws are invariable. The processes of a few years ago are now obsolete, but the principles upon which they were founded will be applied to new methods for generations to come.

To the workers in flotation has fallen the problem of outlining the rudiments, and then by means of laboratory experiments, made by aid of the results of workers in the related sciences, developing flotation to the point where scientific reasoning may be applied to direct tests on ores as is now done in cyanidation. It took twenty years to develop the science of the cyanide process. It will take as long in flotation if we continue our antiquated methods. So far as I can learn, not more than two of the great number of recent contributors of articles on flotation have

[1] From the *Mining and Scientific Press* of September 2, 1916.

had an opportunity for a deliberate study of the related sciences. The rest of us have a job to look after and are busy enough attending to it. Advancement is, therefore, slow. The papers by O. C. Ralston and E. E. Free are, of course, excellent. But in many cases they shoot above our heads; for this we and not they are to blame.

The majority of the workers in flotation who have had the advantage of a school of mines training have taken only the prescribed four years and then hurried into the business of mining. Their love for science was none too great when they left school and the constant employment in the art has in no way tended to increase it. By a careful reading of the articles mentioned they might hope to glean some facts, the knowledge of which would be of aid in the art of metallurgy, but the material is entirely too heavy for one who has not had a special training in science.

We should learn to think—not parrot the statements of others—in terms of the molecules before science will be of aid to us in flotation. We cannot adjust ourselves to this in a moment, it requires time and effort. Many of us have sat aghast while an astronomer spoke of distances in terms of the diameter of the earth. We must now go to the other extreme and become familiar with molecular dimensions. This requires much study, but in it we acquaint ourselves with the observations of physicists and chemists so that we are not likely to spend valuable time in discovering something that is already known.

The mastery of science is not easy. While in school we had to learn the chapters page by page, but this does not seem to be the best way for those without an instructor. To advise one to go through a book rapidly, gathering only an idea here and there, and through it again, may seem to be superficial. But the aim is to master the subject and this is doubtless the way to do it. This method of study is endorsed by Dr. V. H. Gottschalk [2] when he says: "After several readings of the short paper on . . . , read first the excellent summaries at the end of . . . before undertaking a rapid survey of the whole set; follow this by a more

[2] Bibliography, "Concentrating Ores by Flotation," University of Missouri.

careful consideration of the summaries with re-reading of portions of the text when necessary; continue this process until the drift of the argument begins to reveal itself."

One contributor has said that the scientific man has aided little in flotation. Indeed he is correct, and so is the old-timer who says that more mines have been discovered by simple prospectors than by mining engineers. The ratio of those who pursue the right methods to those who have no method at all is as 1 : 1000.

Have any of the big companies put their engineers on retainers so that they could review the fundamentals of science and pursue post-graduate work in a university where they could have access to a complete library? Probably none, because the American business man goes straight for the dollar and must see the wheels turning before he is assured of dividends.

Some of the blunders that have crept into the articles on flotation are a great drawback to those who wish to learn but find their library incomplete. One writer has said, for example, " the cohesion of water varies as the temperature . . . and at the boiling-point there is no cohesion." This statement is misleading. Scientists had this problem pretty well in hand nearly a century ago and knew that surface-tension became zero at the critical temperature and not at the boiling-point, as we ordinarily use this term. Brunner[3] recognized this fact in 1847 and knew that surface-tension decreases with rising temperature until the critical point is reached, when liquid and vapor become identical and surface-tension is zero.

In the Smithsonian Physical Tables, the surface-tension of water at 100° C. is given as 61.5, and nothing is said about boiling-point.

Since critical temperature is so closely related to surface-tension it is obvious that we should acquire a working knowledge of it. At one time it was considered sufficient for us to be able to say that critical temperature was the temperature above which a gas could not be liquefied no matter how great the pressure. This served the purpose for which it was intended, but it is in-

[3] "Physical Chemistry," Ramsey and Smiles.

adequate for us now. If we define it as the temperature at which the surface-tension between a liquid and its vapor becomes equal to zero, and any meniscus or bounding surface disappears, we have added to our knowledge of molecular forces.

It follows that when liquids are near their critical point, for example, condensed gases, they will have small surface-tension, while liquids far removed from their critical point, such as molten metals and fused salts, will have large surface-tensions.

Liquid carbon di-oxide is an example of a liquid that is near its critical point at atmospheric temperature; the critical temperature is 31° C. Its surface-tension is therefore very small unless artificial refrigeration is used.

Mercury, on the other hand, at atmospheric temperature, is so far below its critical point that it would be expected to have a great surface-tension, as indeed it has.

To aid further in getting the relation of critical temperature to surface-tension, I quote from Ferguson.[4] He indicates their relation and the basis on which surface-tension of liquids should be compared, saying: " In earlier researches on the subject, comparisons [of surface-tension] were made at the same temperature, but it was recognized by Schiff that surface-tension should be compared at corresponding temperatures, that is, at temperatures which are equal fractions of critical temperatures of the liquids under consideration." Continuing, we find him stating the relation of critical temperature to boiling-point, thus: " Unfortunately the critical temperature of comparatively few organic compounds have been directly determined, and it was supposed that these conditions were fulfilled at the boiling-point of the liquids examined. If this be the case the ratio of the boiling-point to the critical temperature of all liquids should be the same where temperatures are measured on absolute scale."

The degree of exactness with which this condition is fulfilled is remarkable, as can be seen by an examination of tables published by Ferguson, also those in the " Hand-book of Chemistry and Physics," and elsewhere. They show the value of this ratio cal-

[4] *Science Progress*, January, 1915.

culated from a number of substances of very diverse boiling-points.

An examination of these tables shows that it is a fairly accurate generalization to put

$$\text{Boiling-point} = 0.656 \times \text{crit. temp.}$$

where temperatures are measured on the absolute scale; so that from the boiling-point we can calculate the critical temperature (subject to an error of not more than 5 % in the case of the carbon compounds). For a proof that vapors as well as liquids are regarded as having molecular cohesion, one has only to refer to Van der Waal's modification of Boyle's law.

The toy-balloon theory [5] that each molecule of water is drawn toward the centre of gravity of its mass cannot be taken as a substitute for the accepted theory of surface-tension, for it is not in accord with physicists either here or abroad. They generally agree that the radius of molecular attraction is insensible but finite. They are of one accord in the opinion that " every molecule [6] attracts every other molecule that may happen to be within a certain distance from it, which we denote as the sphere of molecular attraction." In the body of the liquid, this attractive force is more or less neutralized by the fact that the molecule we are considering is surrounded on all sides by others, all pulling in different directions. Hence the combined effort is practically zero. At the surface, however, all the molecules are below it, and there are none above to neutralize the force they exert. There is thus a strong downward force tending to drag the molecule into the surface. This force makes itself manifest in the phenomenon known as " surface-tension " or " capillarity."

Methods of ore dressing today fall under one of two heads, gravitation or flotation. The fundamental law of the former was discovered by Archimedes, that of the latter by Leslie. Archimedes, as we know, while in his bath, noticed the loss of weight of his own body and it occurred to him that any body immersed in a liquid must lose a weight equal to the weight of the liquid

[5] Dudley H. Norris, in *M. & S. P.*, Feb. 12, 1916.
[6] "Molecular Physics," Crowther.

displaced. Leslie, a British scientist, was the first (1802) to give a correct explanation of the rise of a liquid in a tube.[7] Archimedes considered only the force of gravity on known masses; Leslie took into account the molecular force. It is Archimedes *v.* Leslie. Metallurgists have written much on Archimedes' law and very little on Leslie's, the latter having been left to the physicist and chemist.

It is surprising how little attention metallurgists have given to the application of the physical principle discovered by Leslie. Until recently they have been quite satisfied to call it "capillarity" and let it pass. Capillarity has made itself manifest to us in many ways. Richards speaks of it in his "Textbook of Ore Dressing" under the subject of amalgamation. He says that the capillarity of mercury is negative except with those metals with which it easily amalgamates; and the trouble due to grease is familiar to millmen. In cupellation, the lead oxide is drawn into the pores of the cupel, while the lead ignores them and tends to shape itself into a sphere. Were it not for molecular cohesion the resulting silver bead would flatten and become so contaminated by the cupel that its subsequent treatment would be difficult. Galena [8] penetrates the fire-brick of the furnaces in which it is treated. Often a network of small veins of bright crystalline galena is found in furnace-linings. The molecular deportment of galena and litharge is quite different from that of lead itself.

In zinc smelting it is necessary to re-work the "blue powder" because the film of oxide,[9] which coats each particle of zinc, prevents coalescence. The forces that control the films on blister-steel and blister-copper are identical with those that maintain the form of the soap-bubble.

The geologist has studied the bubbles in lava and has found that the vesicles [10] are roughly spherical. This spherical shape cannot be maintained unless the pressure on the inside is greater

[7] Some authorities state that Laplace first developed, about 1807, a theory of capillary action.

[8] "Metallurgy of Lead," Hofman, p. 8.

[9] "Metallurgy of Zinc and Cadmium," Ingalls, p. 526.

[10] "Igneous Rocks and Their Origin," Daly.

than that without. Only surface-tension can account for this excess. He is also aware that if the wick of a lamp touches water [11] the latter rises through the capillaries previously filled with oil, makes the flame sputter, and often extinguishes the light. In the same way water will pass from the coarse spaces of sand or from fissures into the fine capillaries of shale, displacing the oil, which is thereby forced into the sand through neighboring pores. The cohesion that holds together the particles of a crayon and adhesion of the chalk to the blackboard, or of dust to a mirror, are all evidence of molecular force. Many of the examples cited come under " capillarity," but since that is difficult to define and is therefore likely to be used to cloak ignorance, I shall not attempt a definition. Molecular cohesion and adhesion, and probably molecular repulsion, must be studied in detail.

A study of capillarity is of great aid in gaining a conception of the conduct of the molecular forces of cohesion and adhesion that cause some substances to float on the surface of a liquid while others sink. I quote from a high-school book on physics,[12] which, to my mind, gives one of the first lessons in the science of flotation. The discussion is as follows: " We must keep in mind two familiar facts: first, that the surface of a body of water at rest, for example, a pond, is at right angles to the resultant force, that is, gravity, which acts upon it; second, that the force of gravity acting upon a minute amount of liquid is negligible in comparison with its own cohesive force. Consider then a very small body of liquid close to the point *O* (Fig. 1) where water is in contact with the wall of the glass tube. Let the quantity of liquid considered be so minute that the force of gravity acting upon it may be disregarded. The force of adhesion of the wall will pull the liquid particles at *O* in the direction of *OE*. The force of cohesion of the liquid will pull these same particles in the direction of *OF*. The resultant of these two pulls on the liquid at *O* will then be represented by *OR* (Fig. 1). If then the adhesive

[11] "Rôle and Fate of Connate Water in Oil and Gas Sands," R. H. Johnson, Bull. No. 98, A. I. M. E., p. 221; also "Capillary Concentration of Gas and Oil," C. W. Washburn, Bull. No. 93, A. I. M. E.

[12] "A First Course in Physics," Millikan and Gale.

force OE exceeds the cohesive force OF, the direction of OR of the resultant force will lie to the left of the vertical OM (Fig. 2) in which case, since the surface of the liquid always assumes a position at right angles to the resultant force, it must rise up against the wall as water does against glass. If the cohesive force OF (Fig. 3) is strong in comparison with the adhesive force OE, the resultant OR will fall to the right of the vertical, in which case the liquid must be depressed about O. Whether then, a liquid will rise against a solid wall or be depressed by it will depend only

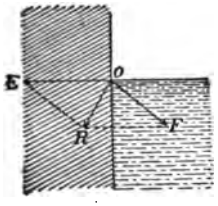


FIG. 1.

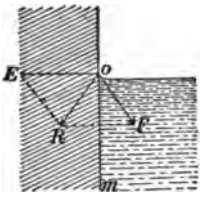


FIG. 2.

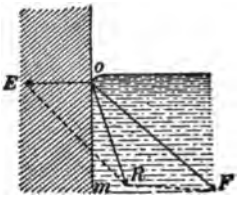


FIG. 3.

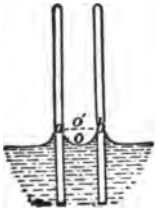


FIG. 4.

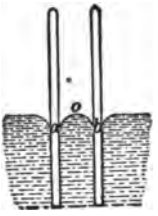


FIG. 5.

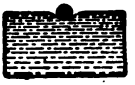


FIG. 6.

on the relative strengths of the adhesion of the wall for the liquid and the cohesion of the liquid for itself. Since mercury does not wet glass [13] we know that cohesion is here relatively strong, and we should expect, therefore, that the mercury would be depressed, as indeed, we find it to be. The fact that water will wet glass indicates that in this case adhesion is relatively strong, and hence we should expect water to rise against the walls of the containing vessel, as in fact it does. As soon as the curvatures just men-

[13] It is a well-known fact that there is a slight adhesive force between mercury and glass and that mercury exerts an attractive force upon air, but the quotation suffices for the present.

tioned are produced, the concave surface *aob* (Fig. 4) tends, by virtue of surface-tension, to straighten out into a flat surface *ao'b*. But it no sooner begins to straighten out than adhesion again elevates it at the edges. It will be seen, therefore, that the liquid must continue to rise in the tube until the weight of the volume lifted balances the tendency of the surface to flatten out. Similarly a convex surface *aob* (Fig. 5) falls until the upward pressure at *o* balances the tendency of the surface *aob* to flatten out."

If, in the case of water against glass, the water is pulled upward and in the case of mercury against glass the mercury is pulled downward, the converse must also be true, namely that in the former the glass is pulled down and in the latter the glass is pushed up.

Now assume that you had two minerals so that they are partly submerged by a liquid and that with one adhesion is very great (relatively) and that with the other the adhesion is very slight. It is obvious that the surface of the liquid will turn up at the contact with the former and down and around the other, and that if these particles are so small that the force of gravity is negligible it is impossible for the former to float and just as impossible for the latter to sink. One of them cannot ride on the surface and is actually drawn into the liquid like gold into mercury, while the other cannot by any means enter the liquid unless its mass is sufficient to overcome the contractile force in the surface of the depressed liquid.

This process of reasoning is what I consider to be a natural and correct result of the study of the cause of capillary rise and depression as presented by Millikan and Gale, and to show that my conclusions are in harmony with their ideas I quote them again, where they discuss the floating of a needle. They say: "So long as the needle is so small that its own weight is no greater than the upward force exerted upon it by the tendency of the depressed liquid surface to straighten out into a flat surface, the needle could not sink in the liquid, no matter how great its density. If the water had wet the needle, that is, if it had risen about the needle instead of being depressed, the tendency

of the liquid surface to flatten out would have pulled it down into the liquid instead of forcing it upward. Any body about which the liquid is depressed will therefore float on the surface of the liquid if its mass is not too great."

If the needle floats, the surface is turned downward, as in Fig. 3, where the resultant of the parallelogram of adhesive and cohesive forces lies in the liquid; and if it sinks, the surface is turned up, as in Fig. 2, where the resultant lies in the solid. Therefore, may we not say that if we can draw the resultant of the forces of cohesion and adhesion when a mineral is in contact with water, we can predict whether or not it is floatable; for if the resultant lies in the liquid (Fig. 3) it will float, and if it lies in the mineral (Fig. 2) it will sink.

We note next that when water is in contact with quartz the resultant lies in the solid; when it is in contact with galena [14] the resultant lies in the liquid. We can, therefore, separate galena from quartz by flotation. I believe it to be quite possible for us to use a contaminating substance in the water and thus vary the molecular attractive forces so that with some sulphides the resultant lies in the liquid and with other sulphides it lies in the solid. This, indeed, has been done, and I believe that this idea is essential to the understanding of selective and differential flotation. To be sure, the introduction of the parallelogram of forces is only a shift from one series of unknowns to another, but it affords a means of stating the problem accurately, which is the first step in a solution.

The reader here exclaims: "Oh well, you are talking about film-flotation?" I think that anyone who will give serious thought to the above demonstration of capillary rise and depression will be convinced that there is nothing but film-flotation.[15] All flotation depends upon the film. If a piece of sulphide is brought to the surface by a bubble, it is, indeed, riding on the wall of a hole in the water, the only difference between this and

[14] Galena and quartz are here supposed to be in such condition that they are typical of floatable and non-floatable minerals.

[15] This statement applies to the processes now in operation, not the orginal bulk-oil method of Elmore.

surface of the liquid. Fig. 7 is a diagrammatic sketch to show this. The surface-tension of the glass-water interface, where the resultant—and therefore the surface-tension—is in the solid, is placed at one end and the curve passes through a zero surface-tension to an extreme point representing tension at the glass-mercury interface.

If the resultant lies in the solid there is no liquid film, but, instead, a surface-tension solid film, and the surface-tension would plot on *ao* in the quadrant *xoz*; while if the resultant is in the liquid there is a liquid film and the surface-tension would be indicated by a point on *ob* in the quadrant *woy*. It seems to me obvious that the non-flotative minerals would plot to the left and the flotative minerals to the right of *zw*, and that such minerals as fluorite, garnet, and calcite, which have been described as at times inclined to float, would be placed very near *zw*.

Since I have said so much about the encasing surface-tension film, it might be well to see if the workers in colloid chemistry take cognizance of this sort of thing. Indeed, we find that there is no lack of precedents. The idea of films around small particles has long since been accepted, and furthermore, before the Wilfley table was invented, they knew that it was the coalescence of these films that caused aggregation. I quote from " Colloid Chemistry " by Ostwald, page 88: " Stress was laid upon the importance of these envelopes in phenomena of condensation early in the history of colloid chemistry. Thus, J. M. van Bemmelen wrote in 1888: ' I think it possible that the formation of the flakes which are precipitated in a liquid is dependent upon a change in the surface-tension of the liquid membranes surrounding the colloid particles, of such type that these membranes between the particles are torn at some point, thus permitting the particles to form aggregates.' "

This excellent picture of aggregation tempts me to quote more of Ostwald's text, but we must leave it and finish the high-school book before taking up a more advanced work. In doing this let us make some simple tests. Touch the round end of a glass rod to the surface of water. No sooner does the smallest physical point come in contact with the water than the water

seems to jump to the rod and spread over the end as if it were magnetized. We say, that is to be expected, that is capillary rise. Observing that there must be a great pressure exerted upon the film that is pulled to the glass rod with such manifest energy, we explain the spreading and consequent rise in the terms of John Leslie, who, in 1802, said: " The result of this pressure if unopposed is to cause this stratum to spread itself over the surface of the solid as a drop of water is observed to do when placed on a clean horizontal glass plate; and this even when gravity opposes the action, as when the drop is placed on the under surface of the plate."

Since this plain and simple reasoning of Leslie's is credited by Clerk Maxwell as being a correct explanation of the rise of a liquid in a tube and, further, since it leads us to the same conclusions as does the " component and resultant " method of Millikan and Gale, we feel an added security and proceed with a similar test using a different solid substance. Let us take for this test a fragment of galena and touch it gently to the surface of the water. Does a dimple appear immediately to indicate the presence of a membrane that is resisting rupture? Not so. The water jumps to the galena much as it did to the quartz, though probably not so vigorously. We argue that this is not in accordance with our expectations; thereupon we repeat the test and make sketches.

Fig. 8 shows how the surface of the water is elevated to wet the glass rod, and Fig. 9 shows much the same sort of phenomenon when galena is used. Though badly confused, we decided to carry the test one step farther. To do this, press the end of the glass rod below the natural surface of the liquid and also allow the galena to float. Fig. 8 and 9 show a cross-section through the contact of liquid and the two solids.

The liquid is now plainly elevated around the rod and depressed around the galena. This seems perfectly natural and satisfactory; but how about the rise of the liquid in Fig. 9 where the galena seemed to be wetted? It is nothing more nor less than adhesion, a component that must be reckoned with, however small it may be, as, for example, in Fig. 3, where mercury is in

contact with glass. Let us prove that there is adhesion between mercury and glass. To do this we will take some mercury in a watch-glass and use the same glass-rod. If we watch closely, as we lower the rod to meet the mercury, we can see that the mercury rises a little around the end of the rod at the instant they come in contact. See Fig. 12. Upon pulling the rod away it is plainly seen that there is adherence. Having performed this experiment we may go into the mineralogy laboratory with a beaker of water and find that any one of a dozen minerals taken at random adheres more or less firmly to water. In some cases,

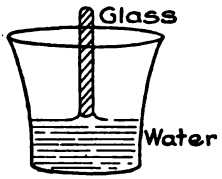


FIG. 8.

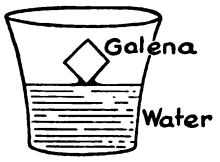


FIG. 9.

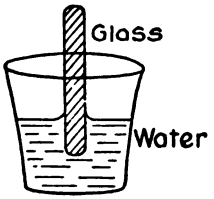


FIG. 10.

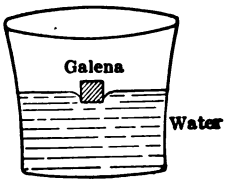


FIG. 11.

when the mineral is pressed below the surface, we can detect capillary rise and in others a depression.

Then what does our popular term " wetting " mean? It can mean nothing more than absence of repulsion unless we give it a special definition, as some physicists have done. As for the spreading, Leslie, the sage of more than a century ago, in speaking of adhesion of a liquid to a solid as indicated in Figs. 8, 9, and 12, said: " the result of this pressure, if unopposed, will cause the liquid to spread." When the adhesive force is sufficiently in excess of the cohesive force the liquid will spread indefinitely, regardless of gravity, until the thickness is such that it could only be measured in terms of the diameter of a molecule. If the

solid body attracts the liquid strongly enough it will draw every particle of it as near as possible to itself. Thus it is that a liquid spreads over certain clean surfaces. But such perfectly clean surfaces [17] are difficult to obtain and that on account of this very phenomenon. Thus, the least drop of oil touching a glass surface spreads over it quickly and completely changes the effect of adding a drop of water. Such deportment needs no emphasis to impress those interested in the laws relating to flotation.

The spreading of a group of molecules of water within the radius of molecular activity of the glass is analogous to the spreading of a ball of soft putty while resting on a plane surface. In both cases the distortion is due to attraction; in the first, the attraction is called molecular; in the second, gravitational.

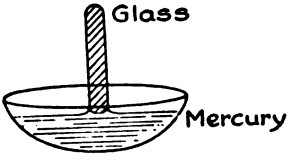


FIG. 12.

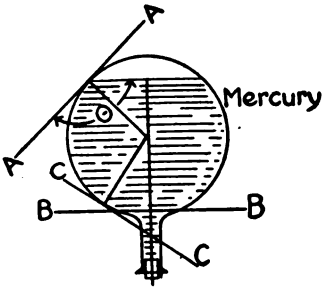


FIG. 14.

But analogies do not satisfy us; we are seeking the foundations of a new and important science, and there will be opportunities for analogies later. Leslie said "if unopposed." We shall do well to deal with components and not generalities. We are reminded therefore how we stated above that in some cases, when the mineral was pressed below the natural surface of the water, we could detect capillary rise and with other minerals a depression. This statement must be considered with caution lest we let important facts slip our attention.

Look again at Figs. 4 and 5. Shall we agree that in contact with a perfectly clean piece of glass the surface of water always turns up and that of mercury always turns down? You say, Yes;

[17] "Mechanics, Molecular Physics, and Heat," Millikan.

that has been proved. Not so; and here, as has often been our experience, we find that we have to unlearn what we have once learned. Let us place a glass rod in mercury so that it will rest in a position, not vertical as in Fig. 5, but in an inclined position, and draw the components of adhesion and cohesion and their resultant. See Fig. 13.

Now we know that the surface of a liquid tends to adjust itself at right angles to the resultant of the forces acting upon it and that if gravity predominates the surface is horizontal. But let us consider a group of molecules at *O* so small that the molecular forces predominate over gravitational forces. We have the force of adhesion *OE* acting at right angles to the surface of the glass and pulling the molecules to it and the cohesion of the liquid pulling these same particles in the direction of *OF*. The resultant of these

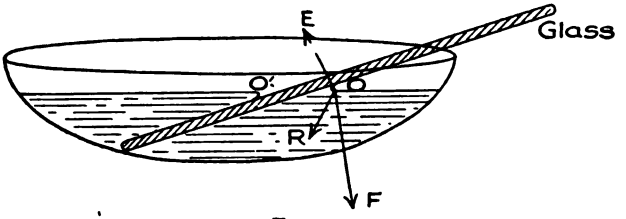


FIG. 13.

two forces, *OR*, is the force to which the surface assumes a position at right angles, and since *OR* lies to the left of a vertical line through *O* it is apparent that the surface of the mercury must turn up to meet the glass. In like manner it can be shown that the mercury turns down to meet the glass at *O'*. Since the mercury turns down at *O* in Fig. 3 and up at the same contact in Fig. 13, it is obvious that there is a slope of the glass at which the mercury would stand level. It may seem bold to draw these components so freely when so little is known of their absolute value. It must be said in explanation that they are only diagrammatic and that is all that Millikan and Gale intended. It is a fact, however, subject to a simple ocular demonstration, that mercury does turn up to meet the glass at *O* and down at *O'*, Fig. 13. The point to be made is that in both cases the resultant lies in the mercury, even though the mercury turns up to meet the glass as does water

against glass where the resultant lies in the solid, and that the slope of the liquid contact must be considered only in connection with the angle at which the mineral meets the original surface of the liquid. The elevation of the mercury at *O* does not mean that the sum-total of all the forces tends to pull the glass down as does water pull the glass in Fig. 4, for we must remember that the film of mercury extends entirely around and under the glass and that it tends to contract and reduce its distorted surface-tension film to a minimum. It will therefore push the glass upward if the downward component due to the weight of the glass is less than the upward component due to the contractile force of the liquid.[18] Briefly stated, an upturned liquid does not always indicate that the resultant turns into the solid as one would conclude from a study of Fig. 2. By the purely theoretical treatment of components adopted in Fig. 13, one can show that the surface of water also may well be approximately horizontal when in contact with glass.

After reaching these conclusions by merely "reading between the lines" of a most elementary physics and checking them by laboratory tests, it is interesting to note that a more advanced text-book [19] gives further corroboration in the recitation of a "test to determine the angle of contact of mercury with glass."

An inverted spherical flask, as shown in Fig. 14, is used. The quantity of mercury in the flask is adjusted until its surface in contact with the glass is horizontal.

Then $\frac{d}{2}=r\cos\left(\Theta-\frac{\pi}{2}\right)$, where Θ is the angle of contact sought, d = diameter of circle of contact of mercury and glass, and r = radius of the spherical flask.

Likewise the surface of water would be about as shown by line *BB*. Contamination of the glass or liquid might well give surfaces that lie anywhere between the two mentioned. This might be called a reciprocal method for determining the angle of contact; for in this test the liquid surface is horizontal and the solid surface

[18] Here the principle of Archimedes, namely, loss of weight due to displaced liquid, is not taken into account.

[19] "General Physics," by Edser, p. 306.

is inclined, while the angle of contact, as we are accustomed to thinking of it, appears with an inclined liquid surface against a vertical solid surface. The " direct " position of Fig. 14 appears in Fig. 15 where *AA* and *CC* are vertical. This shows the same angle of contact in a position more familiar to us.

The foregoing shows that it is insufficient to say that the liquid turns up or down. The angle of contact must be given; it is the same regardless of the slope of the solid surface. For example, in Fig. 13 the angle of contact at *O* must be the same as at *O'* and again the same at *O* in Fig. 3. Again the actual angle of contact may be distorted by the weight of the mass, as when a drop of mercury rests on glass.

The question may well be repeated: Is it correct to speak of a surface-tension film of mercury against glass, and if the term is cor-

FIG. 15.

rect, do we need added evidence that it does exist at the mercury-glass interface?

In our first conception of the film we thought only of the upper horizontal surface of a liquid, that is, the liquid-air interface of standing water. We then extended it to include the walls of a submerged air-bubble, and now the only rational application of film or membrane is to include also all interfaces where there is surface-tension. If there is a solid-liquid interface in which the resultant turns into the liquid, the membrane is in the liquid, and if the resultant turns into the solid, the membrane is in the solid. It is of the utmost importance that we add contaminating substances to the mill-water that will cause the membrane surrounding the grains of ore (sulphides) to be in the liquid and simultaneously cause the membrane around the gangue to be in the solid. Since the solid membrane is an intangible sort of a thing because it is solid, it is best to deal with its antithesis: the absence of a liquid membrane. It may well be said therefore that when the

flotation metallurgist has contaminated his liquid so that there is a liquid membrane around the ore particles and none around the gangue, he has mastered the first step in his process.

The liquid film must not only surround the ore particles, but it must be of such a nature that it will rupture at the point of contact with an impinging air-bubble and thus cause coalescence; or if coalescence does not take place the films must cohere. This is the second step.

Reference to another simple and familiar physical experiment may be of service here to give added evidence that when mercury is in contact with glass the membrane is in the liquid—a state quite different from water in contact with glass—and aid in further acquainting us with laws second to none in their application to flotation, the laws of molecular cohesion and adhesion.

Take two conical capillary tubes, *a* and *b*, Fig. 16. Place

FIG. 16.

mercury in *a* and water in *b*. The mercury will at once run to the large end and the water as quickly to the small end of the respective tubes. The mercury will travel to the larger end of the tube even though it be slightly elevated. In doing so, it decreases its surface and finally reaches the point where the diameter of the tube is sufficient to allow it to assume the form of a sphere. Such conduct is possible only when a liquid is surrounded by a surface-tension liquid membrane. Here, with the mercury, surface energy in the liquid, after its well-known manner, tends to reduce the amount of surface to a minimum. The same components exist in *b*, but they are of different magnitudes and are such that the liquid membrane is only at the liquid-air surface, and it is obvious that it is reduced by a movement toward the small end. The concave water membranes at the ends are similar to the piston of a hydraulic press, and the liquid is drawn in the direction of the greatest force per unit of area. If we assume that these concave surfaces are hemispherical it is

obvious from the formula, $P=\frac{2T}{r}$ that the drawing forces per unit of area toward the ends are inversely as the radii. If the liquid film extended entirely around the water such an increase in the total surface could not happen.

"At a solid-liquid interface two cases are therefore possible—surface-tension in the same sense as in the case of the gaseous bounding medium may appear or," according to Wilhelm Ostwald, " we may have a surface-tension of the opposite character. In this the [liquid] surface does not tend to become as small as possible, and we say that the solid body is wet by the liquid. Mercury on glass is an example of the first; oil on glass, of the second. When the surface of a solid is wet by a liquid, it [the solid] acts like the surface of a liquid, and therefore seeks to become as small as possible."

At this point an analogy may be of value, not as a proof but as an aid, in showing how the deportment of mineral grains in a flotation-cell might well depend on whether they are or are not surrounded by a liquid film.

In this hypothetical case, we grant first that it is a physical fact that glass submerged in mercury is encased in a liquid membrane; that this membrane is squeezing the glass in accordance with the formula $P=\frac{2T}{r}$, in the same manner as if air occupied the hole in the mercury in place of the glass. Second, let us remind ourselves of the great " affinity " of mercury for gold. This affinity or capillarity [20] is well known and one only needs to be reminded that gold is drawn into mercury [21] in the same manner as glass is drawn into water to see that they are perfectly co-ordinate.

We take a pulp composed of mercury, particles of gold, and crushed glass; we place it in a Callow cell and blow air through it. Can you conceive of the gold entering or even clinging to an

[20] In using "affinity" and "capillarity" I am only attempting to use terms that we have all used when discussing amalgamation.

[21] Thomas T. Read, Trans. A. I. M. E., Vol. 37, says that amalgamation is a physical rather than a chemical process; that the surface-tension of mercury draws the gold beneath the surface.

air-bubble? No, you would not think of such a thing any more than you would of the gold in the amalgam on the copper plates mysteriously popping to the surface and parting company from the mercury. But, on the other hand, consider the glass. It is surrounded by a liquid membrane of mercury. If this membrane comes into contact with the membrane of an air-bubble and bursts at the junction, the glass will be squeezed out of its little sack into the large one and ride securely to the surface on the wall of the resulting bubble. Thus the cell would produce an overflow of glass and an underflow of mercury with the gold. If we replace mercury with water, glass with galena, and gold with quartz, and adjust the detail by means of a contaminating substance, we afford a complete and perfect transfer from a hypothetical to an actual operating flotation-cell. Unfortunately, too many of us have concerned ourselves so much with detail—the contaminating substances, etc.—that we have failed to grasp the fundamental idea. Electrolytes, static charges, osmotic pressure, and much of the researches of recent workers in physical and colloid chemistry will all have their places in the science of flotation after the foundation has once been laid.

Archimedes was interested only in the mass per unit of volume, Leslie in the manner in which the molecular forces of a substance affected an unlike substance. Since the range of action of molecular forces is so very small it is obvious that only those molecules at the surface could be sufficiently close to another substance to affect it. We are interested, therefore, in the forces at the common surface of two substances. In this, our position is the same as that of the chemist. Bigelow [22] says, "more and more we are realizing that the conditions in contact surfaces often play the decisive rôle in important processes."

I have tried to expose the fallacy that mineral particles adhere to impinging bubbles; as an alternative, I have advanced a theory involving coalescence, this being more in accord with scientific ideas. We are familiar with the coalescence of two soap-bubbles, but have much to learn concerning the coalescence

[22] "Theoretical and Physical Chemistry," p. 247.

of two films when one of them surrounds a solid. Here I would recommend a study of boiling in the volume on "Heat" in the "Text Book of Physics" by Poynting and Thompson. It teaches that the bubbles which carry the steam to the surface of a liquid do not rise from points at random, but from definite points or particles of foreign matter that form a boundary of the liquid. There must be a nucleus in the shape of a minute bubble into which the steam passes. As evaporation proceeds, the bubble grows and finally breaks away, always leaving a small portion behind as a nucleus, just as part of the neck of a drop of water is left when the drop breaks off from a surface. Some substances carry a great many nuclei while others are barren. A beaker, thoroughly cleansed in hydro-fluoric acid, is so barren of nuclei that water can be raised several degrees above the boiling-point without boiling taking place. A piece of flint immersed in a liquid was alive with bubbles over its entire face until broken in two, when no steam was given off from the freshly formed surface. The introduction of iron filings caused rapid ebullition. Substances over which water is most reluctant to spread, that is, those solids which show the least adhesion for water, furnish the greatest number of nuclei. One paragraph from a paper by Lord Rayleigh [23] where he discusses "Liberation of Gas from Super-saturated Solutions," is sufficient to show the close relation between boiling and flotation. He says: "It seems to me that Tomlinson was substantially correct in attributing the activity of non-porous surfaces to imperfect adhesion. We have to consider in detail the course of events when a surface, for example, of glass, is introduced into the liquid. If the surface be clean, it is wetted by the water advancing over it, whether there be a film of air condensed upon it or not, and no gas is liberated from the liquid. But if the surface be greasy, even in a very slight degree, the behavior is different." In another book [24] we learn that "metal turnings depress the boiling-point because their molecular attraction for water is less than that of glass."

We have ample evidence, therefore, that solids, like fresh

[23] *Philosophical Magazine*, Vol. 48, 1899.
[24] "Theory of Heat," Preston.

quartz over which water spreads freely, do not carry nuclei of air, while solids, like galena over which water does not spread freely on account of adhesion, do have small bubbles attached to them while submerged in water. For an extreme case where air nuclei would be present, we might suppose a glass sphere to be submerged in mercury. As it passes below the surface with its angle of contact of 140°, it would appear as shown in Fig. 17.

With the disappearance of the waist at *a*, the film closes around an air nucleus. A small quantity of air would thus be carried down and if the mercury were transparent, one could see an air-bubble attached to the glass. A fresh piece of glass in water would not do this, for the water would close over it as shown in Fig. 18. But we do not have to go so far afield to ac-

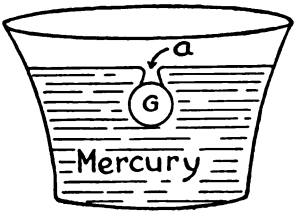


FIG. 17.

FIG. 18.

count for attached air-bubbles. The surface of all minerals contains depressions and it would be impossible for them to pass from air to water without some of the air residing in the depressions being carried below the surface. Whether or not the air is held in place depends on the adhesion of water and mineral. If adhesion is less than cohesion of the liquid molecules, the surface-tension film will pass around the air nuclei and hold them in place, but if adhesion is greater the water will spread over the entire surface of the mineral and ultimately release the air-bubbles. The application of these principles to flotation is simple: minerals with the least adhesion for water will retain the greatest number of small bubbles; these bubbles are inflated by gases expelled from the solution; and finally an air-bubble in its passage impinges against, and coalesces with, the attached bubbles and the mineral is carried to the surface by the resulting bubble,

which is inflated with air and expelled gas. I wish to express my gratitude to Dr. Joel H. Hildebrand for his critical reading of these notes and for his assistance during the seminar in "Colloids and Surface-Tension" at the University of California. Also I wish to thank H. M. Parks and Ira A. Williams of the Oregon School of Mines for their co-operation.

THE ARMOR IN FLOTATION

By Will H. Coghill

As the man of science takes a beam of light and passes it through a crystal prism, and it comes out on the other side of the prism broken up into its components, so we must take each effect in flotation and resolve it into a " spectrum " to reveal the cause.

It has pleased us, from the start, to speak of a pregnant froth as " armored." By this expression we convey the idea of greater stability on account of solid constituents. Are we justified?

At the beginning it is necessary to have in mind the exact physical relation of the film to the mineral grains. In the absence of facts subject to ocular verification I will state what this relation should be when it is the natural effect of causes as I understand them. I believe that a froth gets its load from two sources: first, from grains wholly or partly surrounded while in bulk-water with liquid films which feed the bubbles by coalescence, and second, from mineral grains which become entrapped at the surface of bulk-water, between the ascending bubble and the lower layer of the froth. The chief constituents of the first are sulphides, of the second, gangue or at least minerals on which water spreads freely, and appear as shown in Fig. 1. The first,

Fig. 1.—Froth Laden with Quartz.

if wholly non-wetted, ride upon the surface of the froth just as galena rides the surface of bulk-water in an H. E. Wood machine,

and further, they are on the outer surface, being the solid residue from perished bubbles. If partly non-wetted (perchance these constitute a great portion of the floatable sulphides), the dry spots would tend to prevent sinking while water would spread on the remaining portion. A hypothesis involving a partly wetted surface is justified by the results of physical measurements. I refer to the work of Dr. Huntington, who found that the angle of contact of dark blende on a principal cleavage face was 53° while on another cleavage of the same specimen it was 69°.[1] Again, a part of the surface of the mineral might be old while another part is new—formed in a ball-mill, for example.

In a recent article [2] I called attention to the way in which like floating objects are attracted to each other. Let us take the case of two pieces of galena floating on bulk-water to find the numerical value of this force of attraction, that is, the strength of the armor. They appear as shown in Fig. 2.

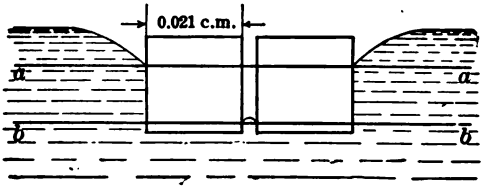


FIG. 2.—Bulk-Water Laden with Galena.

The side pressure above the line *aa* is that of the atmosphere and the same at all points. The pressure below *bb* is that of the liquid in equilibrium. The unbalanced force then must lie between *aa* and *bb*. We know that at all points in the free surface of a liquid, where it is plane, the pressure is the same and is that of the atmosphere, increasing at the rate of one gram per square centimetre for every centimetre in depth.

Assume that the pieces of galena have a length of one centimetre with the cross-section shown (about 65-mesh) and that *aa* and *bb* represent traces of horizontal planes containing the contacts of the three phases. The area subjected to the unbalanced

[1] Trans. Faraday Society, Vol. 1, 1915.
[2] Colorado School of Mines *Magazine*, January, 1917.

force is about 0.01 cm. × 1 cm. = 0.01 sq. cm. The average depth is about 0.02 cm. The total unbalanced hydrostatic pressure is,

$$0.01 \times 0.02 = 0.0002 \text{ gm. or } 0.2 \text{ mg.}$$

It seems apparent then that the unbalanced hydrostatic pressure (0.2 mg.) is such a small part of the tensile strength of the film (70 mg.) that the armor effect from this cause is negligible.[3]

The same method of calculation cannot be applied to sulphides on curved liquid films, but I believe that any effect from a similar cause can be ignored. There is, however, an unquestioned armor effect due to the arching of a solid-liquid mixture with the concave (upward) surface of the film and the containing walls of the flotation machine for skewbacks. The measure of this effect must be left to conjecture.

Quartz (gangue) in the froth must next be considered to see if it has a stabilizing effect. At first thought it may seem that quartz goes into the froth in opposition to the laws of cause and effect. But this view is wrong, and further, the cause producing this effect is perfectly apparent. Too little thought has been given to this phase of flotation. The pyro-metallurgist gives his chief attention to the slag and lets the metals take care of themselves. In flotation we have given all our thought to the sulphides. Let us consider the gangue for a moment. It is indeed a truism that anything in the category from horse-shoes to diamonds can be collected in a froth, if sufficiently small, so that the force of gravity is negligible as compared with the molecular forces of cohesion and adhesion. Please picture the froth-covered pulp in agitation. A rising bubble about to emerge and pass into the froth is separated from the froth by only a thin stratum of pulp, that is, by water with a uniform mixture (if the gangue is not flocculated) of all the constituents of the ore. In an instant the films come together and a portion of the solids are entrapped. Being thus entrapped, it is contrary to the laws of nature for galena to escape the clutches of the liquid film, and

[3] The drawing (Fig. 2) is only an approximation of conditions as they exist on bulk-water, but is, I believe, sufficiently correct to justify the conclusion.

the exit for the quartz is a restricted one, as will be shown later. For galena is repelled from the liquid by the film and obliged to ride upon it and quartz is drawn into the film and made fast between the two surfaces. There is no exception.[4]

It is impossible to practice flotation without entrapping a portion of the solids; these might consist of mineral or gangue in the condition of either galena or quartz, or any of the possible combinations; but whatever the condition, they must conduct themselves as one or the other. It is not at all unlikely that some of the sulphides contributing toward a rich concentrate are entrapped grains in the condition of quartz and therefore held in the film as shown in Fig. 1.

Do such grains add tensile strength to the film? Having proved the inefficacy of forces arising from surface configuration in the one case (Fig. 2) it can be dismissed in this; but a scrutiny of Fig. 1 brings to mind the popular demonstration in physics showing the enormous force with which two discs are pulled together by a drop of water. The demonstration runs about as follows:

"It is a matter of common experience that the hairs of a paint-brush cling together when the brush is withdrawn from the water. The reason is obvious; water clings to the hairs, and the free surface of the liquid tends to contract and pull them together. The force is much greater than the force of surface-tension.

"Let Fig. 3 represent the side-view of two plates with a drop of water between them. The water spreads out into a circular disc of considerable area. Let R be the radius of the flattened

[4] This cannot be over-emphasized. All minerals when classified according to flotative properties (where liquid and air are the fluid phases) come under one of two separate and distinct heads: they either exert an adhesive force greater than a certain minimum so that the liquid spreads upon them with no ultimate increase of surface energy, or, an adhesive force less than this, so that their submergence increases the area of the surface-tension film and therefore the surface energy. In short, a liquid surface-tension film is either absent or present at a solid-liquid interface. Where it is absent the liquid tends to include the mineral. Where it is present the liquid tends to exclude the mineral. I have symbolized the former by "quartz" and the latter by "galena." What I have said applies to vesicles of water inflated with air (a bubble) as well as to bulk-water.

drop; d the distance between the plates, equal $2r$; and let T equal surface-tension of the liquid. Then the total force F urging the plates together is,

$$F = 2\pi \frac{RT}{1} + \pi R^2 T \left(\frac{2}{d} - \frac{1}{R}\right)$$

"If the surfaces are true planes, the discs will approach each other until d becomes exceedingly small, and the force exerted may be sufficient to fracture them."

This formula cannot be applied to the problem before us because the conditions, so much alike in some respects, are so different in others that the conclusions would be misleading. An acquaintance with the method of derivation is necessary in order to appreciate this. The water between the discs is under a dila-

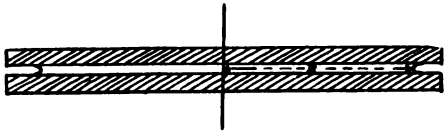


FIG. 3.—Parallel Plates with a Drop of Water between Them.

tional strain due to its tendency to spread. The water between the mineral grains in Fig. 1 is also under a dilational strain, but the strain in this case is due to the weight of the column of water reaching along the films to the surface of bulk-water. It is as if the water-filled opening between them were connected to a water-surface through a suction-pipe. There is an interesting analogy in a discussion of regelation that reads as follows: "When two blocks of ice are placed loosely together so that the superfluous water which melts from them may drain away, the remaining water draws the blocks together with a force sufficient to cause the blocks to adhere." If the water were drained away from the ice through a draught-tube the analogy would be perfect. Having thus stated the problem, the calculation is simple. Assume that the vertical length of this draught-tube is 25 cm. (about 10 in.), the depth of the froth, using grains of the same dimensions as before, and we have as a difference between inside and outside pressure due to the weight of water sustained,

$$0.021 \times 25 = 0.525 \text{ gm., or } 525 \text{ mg.}$$

while as before the tensile strength of the surface-tension film (two surfaces) is about 70 mg. A temporary armor, at least! I say " temporary " because the rough surface presented in Fig. 1 is not one of minimum potential energy. If anything tends to disturb the equilibrium it must be considered. There is one thing. I refer to the weight of the column of water sustained and believe that it would tend to slip the quartz grains along the film to bulk-water. As a result the skewbacks for the arch would be continually dropping back into the water (see Fig. 4), at a rate depending on viscosity and other factors. The weight of the grains themselves would also tend to produce this slipping. As for viscosity, we know that quartz would drop back faster in a film of low viscosity and that viscosity decreases with rise of temperature. Heat should therefore improve the grade of con-

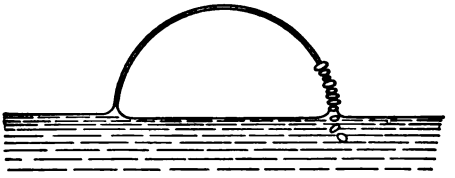


FIG. 4.—A Bubble Spilling Quartz Back into the Water.

centrate. While there might well be causes which would neutralize this effect it is interesting to associate, in this connection, a paragraph from Dr. Gahl's paper [5] that reads as follows: " How can we raise the grade of our concentrates—that is, reduce the percentage of insoluble matter contained in them—without entailing additional copper losses? We know from laboratory experiments that this can be done by expensive methods, for instance, by heating the solutions." Would not heating the froth only, with steam-coils, effect the same advantage at much less cost?

By the use of fundamental principles of physics I have adduced considerations that are in accord with colloid chemistry, namely, solids armor a froth. To justify this conclusion, I quote from W. D. Bancroft: [6] " We cannot get a froth with a pure

[5] Bull. A. I. M. E., Sept., 1916, p. 1675.

[6] *Met. & Chem. Eng.*, June 1, 1916, p. 634.

liquid and air. There must be present a third substance in colloid solution." Again Mr. Bancroft says that we call a phase " colloidal " when it is sufficiently subdivided, not limiting ourselves definitely as to what degree of subdivision.[7] He states that a sufficiently subdivided phase stabilizes a froth. In so doing he has stated the effect. I have tried to point out the cause.

If the impression given by Fig. 1 is that what I have said about stabilizing causes applies only to coarse mechanical suspensions, that is, where the diameter of the discontinuous phase is greater than the thickness of the film, it should be made clear that suspensions of all degrees of dispersion (diameter of the solid) are included. Wolfgang Ostwald's [8] discussion of internal friction of suspensoids justifies this conclusion. He says: " It may be regarded as typical of suspensoids that their viscosity is but slightly greater than that of their pure dispersion mediums. It must be remembered, however, that this is true only when such systems are dilute. In concentrated form the mass of the disperse solid phase may predominate over that of the dispersing medium, as when powders are merely moistened so as to be coated by a thin but continuous liquid membrane. Such systems may be so viscid that their properties approximate those of solids. We need but recall how moist sand may be cut into slices, and the rigidity of the scales and crusts of dried colloid metals. From this it follows that with increase in concentration the viscosity of a suspensoid rises very slowly at first, but very suddenly and greatly at high concentrations." What I have indicated in Fig. 1 is equivalent to the " slice " mentioned by Ostwald. It is not necessary for the armor to extend over the whole surface of the froth in order for it to have a stabilizing effect.

When the discontinuous phase has such a high degree of dispersion that the conditions approach those of a molecular solution (soap in water is an example) there is a new set of forces to be considered. This has been described and called " adsorption."

One has only to shake finely crushed ore in a test-tube with

[7] "The Flotation Process," by Megraw, p. 28.

[8] "Handbook of Colloid Chemistry," by Ostwald, p. 146.

water to see that the solids lend persistence to the bubbles, though in some cases the bubbles taken collectively may not be sufficiently voluminous to constitute what is ordinarily styled a froth. There is nothing new about this. T. K. Rose [9] says: "Losses in amalgamation are also caused by greasy substances contained in some ores, such as the powdered hydrated silicates of magnesia and of alumina, which cause frothing."

Rose says "greasy." This would indicate that the galena type of mineral is the greater stabilizer. On the other hand Gahl [10] thinks that the frothing characteristics follow the tailing-pulp. We must, some day, learn more about this. Taggart and Beach [11] are doubtless justified in their statement that "the formation of a scum of floated sulphide increases the stability of the float," but when they say, in discussing adsorption and surface-tension, "On philosophical grounds it is impossible to consider that a real physical discontinuity occurs at the boundary between two media. In other words there must be a very thin layer of transition in which there is a rapid but continuous change in the concentration of the components," they are perpetuating an early conception that has been more befogging to me than anything I have read relating to this subject. After being so perplexed by the frequent recurrence of this statement in the various texts, it was indeed a delight to read from the pen of Irving Langmuir in a paper [12] that impresses me as epoch-making in the studies of surface-tension, as follows: "The surface of a solid (or liquid), therefore, does not contain, as is usually assumed, a transition layer, consisting of several layers of atoms or 'molecules,' in which the density varies by continuous gradations from that of the solid to that of the surrounding gas or vapor. Instead we find that the change from solid to empty space is most abrupt. In a sense, the re-arrangement of the atoms, in the surface layer, causes this layer to assume the character of a transition layer, but the density of the packing of the

[9] "Metallurgy of Gold," by T. K. Rose, p. 207.

[10] Bull. A. I. M. E., Sept., 1916, p. 1680.

[11] Bull. A. I. M. E., Aug., 1916, p. 1382.

[12] "Constitution and Fundamental Properties of Solids and Liquids," Journal of American Chemical Society, Nov., 1916, p. 2249.

atoms in this layer is undoubtedly greater than in the body of the solid, so that there can be no gradual change in density from that of the solid to that of space." Mr. Langmuir's conception impresses me as consistent, the other not.

There is yet another thing to be said about a bubble with grains deposited between the films as shown in Fig. 1, to wit, the space between the grains is a repository for water. A wet froth would therefore accompany a low-grade concentrate. Indeed this seems to be in accord with observation. For example, " Toward the tailing end of the flotation machines," says Dr. Gahl, " most of this dark material has disappeared and the froth is lighter and of a more watery nature."

THEORY OF ORE FLOTATION [1]

By H. P. Corliss and C. L. Perkins

The physics and chemistry of ore flotation constitute the subject of extensive literature, but no one contribution presents an explanation of all the physico-chemical factors involved.[2] These articles [3] include collectively considerable information of importance, but have failed to elucidate this very obscure problem.

In this paper is presented an explanation of the actual factors involved in ideal flotation and also of other practical observations incident to the art. The theory presented herein has been substantiated by actual experiment, but only a brief résumé of the experimental results is included.

The greatest success in the art has been obtained in processes in which a gas, usually air, is introduced into the pulp, either by chemical means from carbonate and acid (Potter-Delprat process), assisted by vacuum (Elmore process), by the use of agitation (Minerals Separation process), or by blowing it in through a porous blanket (Callow process), and with or without the use of oil. The explanation offered in this paper is for this type of process especially, although the simple flotation-principles involved in such processes as the Macquisten, the Wood, and the bulk-oil process, are included. In all these processes the material floated must not be wholly wet by the water or solution in the presence of this gas or the material surrounding this gas, for ex-

[1] From the *Mining and Scientific Press* of June 9, 1917.

[2] *Jour. Ind. & Eng. Chem.*, May, 1917.

[3] See especially the following: W. D. Bancroft, *Jour. Phys. Chem.*, 19 (1915) 275; Ralston, *M. & S. P.*, Oct. 23, 1915; Callow, Bull. A. I. M. E., Dec., 1915, 2321; Anderson, *Ibid.*, July, 1916, 1119; and Taggart and Beach, *Ibid.*, Aug., 1916, 1373. For a very complete bibliography, see School of Mines and Metallurgy, Univ. of Missouri, Bull. 8, No. 1, 1916; also Bull. A. I. M. E., 1916, 1131.

ample, an oil-film on the bubble-surface. If the material is completely wet by the water, it will not float, which is the case of the ideal gangue, while the material floated must go to the interface water-air bubble or entirely into the phase other than water, that is, the oil on the air-bubble.

The relations of the forces acting to produce this result were first stated by Freundlich,[4] and enlarged upon by Hoffman [5] and Reinders.[6] They were first stated for the behavior of a sol, which will be called disperse phase 3 in liquid 1, when shaken with an immiscible liquid 2. Let

$T_{1\,3}$ = interfacial tension between phase 3 and liquid 1;
$T_{2\,3}$ = interfacial tension between phase 3 and liquid 2;
$T_{1\,2}$ = interfacial tension between the two liquids;
If $T_{2\,3} > T_{1\,3} + T_{1\,2}$ the sol will remain unchanged;
If $T_{1\,3} > T_{2\,3} + T_{1\,2}$ the disperse phase 3 will go entirely into liquid 2;
If $T_{1\,2} > T_{2\,3} + T_{1\,3}$ the disperse phase will collect at the liquid-liquid interface and will, if possible, separate the two liquids from each other.

If, however, no one interfacial tension is greater than the sum of the other two, then the disperse phase will collect at the liquid-liquid interface, but the three phases will meet at a certain contact-angle. The application of these principles to flotation may now be stated, for while the greater part of the material floated is much less disperse than that which is considered colloidal, the interfacial tendencies are the same, it simply being a question whether the forces holding the mineral to the interface are sufficient to overcome gravity, if the particle is to float.

Methods of flotation without resort to the use of oil are exemplified in the well-known Potter-Delprat process, in which CO_2 is generated in the acid pulp, but may be carried out successfully on some ores in a Callow cell, using air. Here, if flotation is to result, the mineral must go to the interface water-gas and be

[4] *Kapillarchemie*, 1909, 137, 174.
[5] *Zeit. Phys. Chem.*, 83 (1913), 384.
[6] *Kolloid Zeit.*, 13 (1913), 235.

carried at this interface to the top of the pulp. The word water will be used mostly to denote the aqueous phase, whether it is pure water or a solution, and the floatable material will be called sulphide, since this is the common case. On the basis of interfacial tensions, where if

$T_{s\,a}$ = interfacial tension sulphide-air (or CO_2),

$T_{s\,w}$ = interfacial tension sulphide-water,

$T_{w\,a}$ = surface-tension water-air (or CO_2),

either (1) $T_{s\,w} > T_{s\,a} + T_{w\,a}$ or (2) no one interfacial tension is greater than the sum of the other two, must be true. It is obviously impossible to have $T_{w\,a} > T_{s\,a} + T_{s\,w}$ as the latter two are very large in comparison with the first, according to theoretical reasoning and measurements.[7] Case 2 is the actual one, as can be seen if a drop of water is placed on a flat sulphide surface. Here the water does not spread over the entire surface, but comes to equilibrium with the three phases, sulphide, air, and water in contact at a certain angle. Case 1 would require that the water should not wet the sulphide at all in the presence of air. In flotation then the sulphide comes to the air-water interface and sticks through the bubble-surface to a certain extent, or is held in such a way that the three phases are in contact. The gangue material is completely wet by water and does not float, that is, $T_{g\,a} > T_{g\,w} + T_{w\,a}$.

Some measurements were made to get an idea of these interfacial tendencies, by a method explained in connection with Fig. 1. Here a flat-ground mineral-surface was placed vertically in water or other solution as shown. By raising and lowering the mineral, a quite constant result was obtained for the rise of the meniscus against the mineral above the general level. Here the meniscus was always upward, showing a greater preference of the mineral for water than for air. In the case of the sulphides, when they were raised, the meniscus would soon draw back to a definite height, leaving the sulphide surface above quite dry. For gangue the water does not draw back quickly, but remains, wetting it for some time. The sulphides are proved interfacial

[7] Hulett, *Zeit. Phys. Chem.*, 37 (1901), 385. Also the surface-tensions of molten metals and fused salts are high.

in this way, and the measurements of the height of the point of contact above the general level are interesting. The measurements were made with a cathetometer.

Material.	Water, mm.	0.1% H_2SO_4, mm.	0.1% NaOH, mm.
Chalcocite	1.55	2.10	3.07
Chalcopyrite	2.60	2.50	2.90
Gangue (silicate)	3.20	3.25	3.30

The figures for the gangue are not at the point of contact, for there is none, since it is thoroughly wet by water, but are at the point where the meniscus becomes parallel to the face of the mineral surface. The mineral giving the smallest rise should be the most interfacial and the best floating. This was found to be true, for, without oil, chalcocite is a better floating mineral than chalcopyrite, at least for the ores that were tested. The figures above also show that in alkaline solution a very poor float should be made, as the rise is almost as much as for the gangue. This was also found to be true. Differences even among sulphides are clearly shown, hence it is not surprising to find all gradations in floating properties among ores. These measurements, made on large pieces of mineral, with ground and partly polished surfaces, may not correspond exactly to those for an ore-surface, though in the cases mentioned they were found to give results agreeing with practice.

Another point noticed in these measurements, which is an important one, is how quickly the water is displaced from a mineral-surface when brought in contact with air. If an air-bubble comes in contact with a sulphide particle immersed in water, it must partly displace the water from the sulphide rather quickly if it is to be floated in a pneumatic cell. This was tested for the same minerals, by noting the time taken for the solution to come back to the final point of contact, when the mineral was raised, with the following general results:

(1) Water and acid solutions are removed more quickly in air from chalcocite than from chalcopyrite.

(2) Little difference is noted between acid and neutral solutions.

(3) Alkaline solutions are removed very slowly from all sources.

(4) All solutions adhere strongly to gangue.

These facts also agree with the practical results mentioned above. The success of the Potter-Delprat process may well be due to these facts, since the CO_2 is generated in contact with the sulphide, and time is given for the solution to be partly displaced by the gas or, in other words, for the sulphide to attain the interfacial condition and be floated. When a soluble frothing-agent is used, without oil, the same principles apply, the frothing-agent simply modifying the water to a certain extent.

The use of oil introduces several new factors which make the problem more complex, but the same principles apply. The sulphides can now be interfacial between water and air as discussed above, but, in addition, may be interfacial between water and oil, or even go into the oil-layer. This oil-layer is on the bubble-surface and the forces holding the sulphides to this surface, if it has an oil-film, are much greater than when no oil is used. This point will be proved a little further on. The oil-layer on the bubble-surface need be only of minimum thickness to act, in contact with water, the same as a layer of oil on water as far as interfacial tendencies are concerned. Let

$T_{s\,w}$ = interfacial tension sulphide-water;
$T_{s\,o}$ = interfacial tension sulphide-oil;
$T_{o\,w}$ = interfacial tension oil-water.

Then, if (1) $T_{s\,w} > T_{s\,o} + T_{o\,w}$, the sulphide will go into the oil-layer completely; (2) no one interfacial tension is greater than the sum of the other two, the sulphide will go to the oil-water interface, and the three phases will be in contact at a certain contact-angle. The gangue is thoroughly wetted by water, that is, $T_{g\,o} > T_{g\,w} + T_{o\,w}$.

These inequalities have been stated and applied to the flotation process by Ralston.[8] The second condition given above,

[8] *M. & S. P.*, Oct. 23, 1915.

where the sulphides are interfacial, seems to be by far the most general, though the first condition may be, and probably is, realized, especially when tarry oils are used, which, in grinding with the ore, coat the sulphides more or less with this tarry material. It is doubtful if the lighter oils or the lighter constituents of a tarry-oil mixture film the sulphide at all in grinding, but rather it is probable that this oil is emulsified in the operation. The condition where the mineral is completely filmed by oil would be the best floating condition, and this could be realized in the flotation-cell, where this film would be continuous with the oil-film on the bubble-surface. All gradations of the interfacial conditions

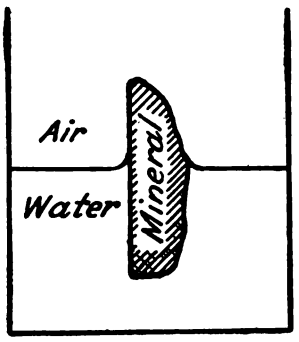


Fig. 1.

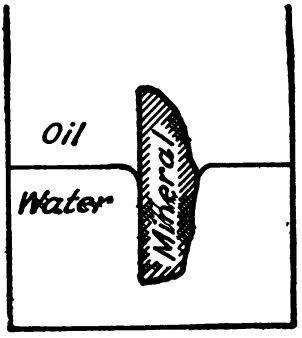


Fig. 2.

are possible, from those that show only a slight tendency to be wet by water in the presence of oil, to those that are thoroughly wet, which is the case of the gangue material.

Experimental determinations of the interfacial tendencies of various minerals were carried out in the same way as described above, except that in this case the interface was oil-water or aqueous solution. In Fig. 2 is represented the case of a sulphide surface at this interface. The floatable materials were all interfacial, and the sulphides showed a decided preference for the oil. This is an important point in showing that the same sulphides are much more strongly held to an oil-covered air-bubble than to one not so covered. In Fig. 1 the sulphide, while interfacial, shows a preference for water over air, and would easily be displaced in actual flotation from the interface and go back into the water. In Fig. 2 the meniscus is now pushed downward into the

water, instead of upward, hence the sulphide is held much more strongly to oil than to air.

The following measurements were made after the meniscus had come to the true point of contact of the three phases, and this point was closely the same, whether the mineral was first wet with the oil or solution. The averages of these two figures are given. Kerosene and a kerosene pine-oil mixture were used mostly, as the interfaces are better defined, especially in acid and alkaline solution, than with many actual flotation oils. These other oils act in the same way, however.

DEPRESSION OF MENISCUS: KEROSENE AND CHALCOPYRITE

Water	0.1% H_2SO_4	1% H_2SO_4	10% H_2SO_4
2.99 mm.	2.02 mm.	1.32 mm.	0.75 mm.

Calcite in contact with neutral, acid, and alkaline solutions and kerosene showed interfacial tendencies in alkaline solution only. Malachite exhibited a small interfacial tendency, except in alkaline solution in which it was thoroughly wet by the solution.

KEROSENE AND PINE-OIL AND AQUEOUS SOLUTION

This was a flotation mixture of 90% kerosene and 10% pine-oil.

Solution.	Depression of Meniscus.	
	Chalcopyrite, mm.	Chalcocite, mm.
Water	3.10	3.42
0.1% NaOH	1.98	2.54
0.1% H_2SO_4	1.45	2.95

Gangue-material in all cases is thoroughly wet by the solution, especially if it is wet by the solution before coming in contact with the oil, as is the case in actual flotation. The case of chalcocite in water, given above, is almost a condition of complete wetting by oil. These experimental results in every way justify the theoretical discussion given, and also show that alkali and acid lower the interfacial tension sulphide-water as the preference for oil is not as great in these solutions as in water, although the sulphide is still distinctly interfacial and hence can be easily floated from acid or alkaline pulps. These results were obtained

by the use of a clean sulphide-surface, but in actual flotation this may not be true for all the particles, and since the interfacial properties are a function of the surface only, one may expect many differences from these ideal measurements. In alkaline solution, for example, there may be some of the mineral which, like calcite, is more interfacial in this solution than in water, and hence would float, although it would not do so in a neutral pulp. In tests it has been found with some ores and oil-mixtures that in an alkaline pulp a better recovery was made in the usual length of time than by prolonged flotation in neutral pulp. This might be true also in an acid pulp for some minerals.

It has been noticed that some surfaces have a strong tendency to hold fast to the liquid first wetting them and not to allow it to be easily displaced by another liquid. In the work upon interfacial tension, described above, such a surface would show a great difference in preferential action or angle of contact, dependent upon whether it was wet with oil or water first. It has also been observed that it is principally those substances having smooth or shiny surfaces which float, while those having dull or rough surfaces do not float. These observations and others point to the following explanation of the mechanism of this action: there is first the inherent property of each substance to adhere to oil or to water to a certain degree. When the substance is brought to the interface between water and oil, these forces tend to come to equilibrium with the third force, the interfacial tension between oil and water, at some definite contact-angle. Here is where the physical nature of the solid surface comes into play. If the surface is smooth and shiny, such as that of a polished metal or a freshly fractured sulphide crystal, then the liquid first touching it is easily pushed back to the position of equilibrium. If, however, the substance has a dull, that is, a capillary surface, so that the liquid first wetting it is strongly held in its pores, then, when it is brought to the interface it may exhibit no interfacial properties at all, although, if it were smooth, it might even show a preference for the other liquid. This shows the reason for the difference, or hysteresis, of the contact-angle noted for some surfaces. It also explains why a particle having such a surface, if first wet with water, as is the case in flotation, will be very diffi-

Numerous data of this kind are given by Lewis [11] and Shorter and Ellingsworth [12] on the action of dyes, salts, and soap. The drop-number apparatus used was the same as described by Shorter and Ellingsworth. Their work also shows that soap and alkali together are extremely active in lowering the interfacial tension oil-water. This would be the condition in an alkaline pulp, as there would then be free alkali and some saponified material with many of the oils used.

The results when colloidal material is present are subject to great variation, due to different speeds of formation of drops. The figures given above for these materials approach the dynamic value, as the rate of dropping was fairly rapid. The static values are much smaller, and are interesting in connection with the emulsifying power of these substances. As an example of this the following result on coke-oven oil against 0.005% hemoglobin solution is given. The time is for the total number of drops formed.

Time.	Drop No.	Interfacial Tension, Dynes per Cm.
2 minutes 40 seconds.....	22.5	13.2
1 hour 4 minutes.....	84.0	3.5

It is seen from the table above, that besides NaOH itself, any salt that hydrolyzes to give an alkaline solution lowers the interfacial tension, and all these salts are beneficial to flotation.

The behavior of the oil at the bubble and sulphide surfaces has been given. In the pneumatic cell this oil is supplied by an emulsion or a coarser suspension of oil in water. In the agitator-type machine, the oil may be beaten in at the cell, though it is also customary to grind the oil with the ore. In either case the problem of emulsions comes in. In the pneumatic process this emulsion is formed in the grinding and must be good enough to last throughout the float, yet not so good as to fail to break down with sufficient rapidity to give free oil for the bubble-surface.

[11] *Zeit. Phys. Chem.*, 74 (1910), 619.
[12] Proc. Roy. Soc. 92 (1916), 231.

The subdivision of the oil is such that no doubt almost all degrees of dispersion exist; the larger droplets may be of sufficient size for one to coat a fair area of a bubble-surface, but the better emulsified portion is of such size that many particles have to unite to give oil enough for the minimum thickness of an oil-film to spread over even a square centimetre. This can be calculated from the minimum thickness of an oil-film [13] and the size of the particles in an ordinary oil-emulsion.[14]

Experimental evidence on these points is conclusive. If a coarse suspension of oil be made simply by shaking the ore, oil, and water together in a bottle by hand, and then put in a small Callow cell, only a partial float results, and the operation must be repeated several times, adding more oil each time, in order to get a good recovery. If, however, too good an emulsion is had, a poor recovery results. For this purpose a kerosene pine-oil mixture was emulsified with water in a De Laval emulser and allowed to stand overnight, and a middle portion of this emulsion was removed for the tests. This emulsion added at the cell gave a small float at first and then stopped. On adding a little acid no further float resulted, but, by allowing the pulp to stand for a few minutes, an additional amount of sulphide was raised, and finally a good recovery was made, though considerable time had to be given for the emulsion to give up its oil. This was also found to be true for another oil that gave an excellent emulsion on simply adding it to water.

It is interesting to note that in these cases it was proved that it was not necessary to grind the oil with the ore, but, by adding it as an emulsion prepared by itself, as good a recovery results. This probably is not true for oils containing tarry matter as explained above. It was also noticed in using the second emulsion, named above, that flocculation of the slime took place in neutral solution, and that these then floated to a large extent, giving a non-preferential float; when, on the other hand, the emulsion was broken by acid and alum, a good preferential float resulted. It was found that this slime in neutral pulp had

[13] Devaux, *Loc. cit.*

[14] Ellis, *Zeit. Phys. Chem.*, 80 (1912), 597.

flocculated with the oil-emulsion so that, on standing, all the oil was carried down, though the emulsion was not appreciably broken.

The value of acid and salts having a polyvalent cation has been demonstrated in some cases, usually in connection with the Minerals Separation type process. In this process there is greater danger of getting too good an emulsion than in the Callow process, and the value of acids and salts of this type consists in their power of breaking down an emulsion, or preventing too good a one being formed. These salts should be used in acid solution, or, otherwise, due to hydrolysis, the insoluble hydroxides formed, for example, $Fe(OH)_3$, and $Al(OH)_3$ have the opposite effect, namely, of preventing the breaking down of the emulsion or promoting its formation.[15] Oil-emulsions in $FeCl_3$ solution, on standing, give a yellow flocculent precipitate, but the emulsion is not broken. The mechanism of this is discussed by Ellis.[16] In a neutral, pneumatic, Callow float, such salts have been found to be harmful. If salts of iron or aluminum are present in the feed-water then acid may be necessary to prevent this action between them and the oil-emulsions.

The value of alkalies has been discussed as giving a better oiling of the bubble-surface. In connection with emulsions, however, a greater effect can be ascribed to the action of alkalies or salts which hydrolyze to give an alkaline reaction, and to those which have a polyvalent anion. If a neutral ore-pulp is shaken with a small quantity of an oil-emulsion it is found that the slime is coagulated with the emulsion and settles out, often leaving the liquid quite free from oil-emulsion. The emulsion is not broken, but simply carried down with the flocculated slime. If alkalies are used, or salts such as last mentioned, then the slime is deflocculated in the great majority of cases. It then settles more slowly, and when it has settled the emulsion is left free and still standing. This is important, for now the emulsion is free to function as it should, that is, to give oil to the bubble-surface. The ore-particles, both sulphide and gangue, are also free to show

[15] Briggs and Schmidt, *Jour. Phys. Chem.*, 19 (1915), 478.
[16] *Zeit. Phys. Chem.*, 89 (1914), 149.

their own behavior toward the water and the oil. This deflocculation should, and does, result in a higher-grade concentrate and a greater and quicker recovery, since now no sulphide-particles are coagulated with, or surrounded by, gangue-particles that prevent their flotation.

The use of lime has not been found to be as beneficial as that of NaOH. This is explained by the fact that this substance, owing to the predominating effect of the calcium ion, coagulates instead of deflocculating the slime, and hence part of the emulsion is removed and the individual particles are not free to float as they should. This coagulating action may be more noticeable in a Callow cell than in a cell of the Minerals Separation type, as in the latter the coagulated slime may be broken up considerably, but the tendency is the same in either case.

The principles involved when varying quantities of oil are used, is a question on which there is great difference of opinion. From theory there should be no difference whether a large or small amount of oil be used, provided the oil is properly emulsified. If a large amount, 2% or 3%, be used, and is not emulsified sufficiently, the excess may float and be of disadvantage in several ways. To test this point a float was made with an amount of oil equivalent to 2% of the weight of the ore, emulsified in a De Laval emulser, and added at the cell (Callow), and a float made. It behaved in every way the same as when 0.2% or less of oil was used, and the recovery was better, with as high a grade of concentrate. Of course, economy would settle the minimum amount of oil to use. This was repeated with other oils and ores. The extra amount of oil used gave a greater oiling of the bubble-surface, and in fact these floats were better than when alkali was used to make the smaller amount of oil more efficient.

In the light of the above work the question of flotation "poisons" was taken up with the idea that any substance which will prevent the breaking down of an emulsion or coalescence of oil droplets, or which gives adsorption of colloidal particles at the oil-water interface, is harmful to flotation. In the first two cases the proper amount of oil will not be freed, and in the other case the oil-surface, if formed, would be covered by an adsorbed layer,

so that no oil-surface would be presented for attachment of the mineral. Experimental work, by actual flotation, had shown what substances, including many dyes, were harmful. Solutions of these substances of 0.01% strength were shaken in test-tubes, with about 2 c.c. of oil, for a few minutes, to the same extent and at the same time. The tubes were then placed upright and the amount of emulsification and the rapidity of coalescence of the oil droplets rising to the top noted, with the following results:

(1) Slight or no emulsification and rapid coalescence of droplets when using methylene blue, safranine, and bismarck-brown. These dull dyes really act like salts, and are not colloidal, nor are they harmful to flotation. In fact, these dyes assist slightly in breaking an emulsion.

(2) Extremely slow coalescence of droplets, the finely divided oil-layer lasting for several hours to days, when using congo-red, bengo-azurin, azo-blue, saponine, tannic acid, waste sulphate liquor, hemoglobin, and eosin. These substances are all injurious to flotation. Most of these are negative colloids. Hemoglobin is highly colloidal, and positive, and its adsorption is probably enhanced because it is oppositely charged to the oil-emulsion. Several of this last class of substances, especially saponine, gave marked emulsification, even with the small amount of shaking received. Some of these substances also form quite stable and viscous skins at oil-surfaces. Another experiment consisted in dividing an oil-emulsion into two parts, to one of which tannic acid was added, and then frothing over equal volumes of each in a small cell. The one to which tannic acid had been added contained 3.5 times as much oil in the residue or tail-water as the other. This shows that the oil-emulsion had been kept from breaking down, and the oil from being frothed over. Besides the substances given above, the injurious effect of insoluble hydroxides of the heavy metals has been explained under emulsions. Other inorganic colloids have been found to be injurious, for example, when floating with $K_4Fe(CN)_6$, the $Cu_2Fe(CN)_6$ formed from the oxidized and soluble copper hurts the float very noticeably. The experimental evidence proves that the action of these col-

loids is, without doubt, as stated, though they may also adsorb at the solid surfaces, and in that way cause a poorer result to be obtained. It is easily seen how the water used in flotation and the slime coming from certain ores have great effect in flotation. This has caused some to say that it is the gangue that determines the success of the process, and, if the water-supply be included in this, they are to a certain extent correct.

The froths produced in flotation are useful as a mechanical means of removing the mineral brought up by the bubble. The formation of a froth, and its stability, are due principally to dissolved materials in the water which give to the solution a variable surface-tension. The static surface of a solution has a lower tension than a fresh surface, whether the substance added lowers or raises the surface-tension of the solvent. Since a large lowering may be caused by a small amount of solute and only a small rise may be obtained, the best frothing-agents are those that lower the surface-tension. Pine-oil is used to a large extent for this purpose in practice, the soluble portion causing a considerable lowering of the surface-tension of water. In many articles that have appeared on the theory of flotation, it has been stated that oils lower the surface-tension of water. This is not very clearly stated, since, as ordinarily understood, oil is insoluble in water, and only soluble material can affect the surface-tension of water. Besides the soluble portion of pine-oil, a part of many other flotation oil-mixtures is soluble and gives a froth. Terpineol, menthol, and many such substances are powerful frothing-agents. The lasting qualities of a froth, as stated above, are due to its variable surface-tension, for if a bubble starts to thin out or to break at a certain point this fresh surface has a greater surface-tension than before, hence is automatically strengthened at this point and resists rupture. In using alkalies it is observed that a more quickly breaking froth results in a pneumatic cell. This can be explained by the fact, as stated before, that a greater extent of bubble-surface is covered with oil, hence there is less surface which contains only the adsorbed frothing-agent, and since oils themselves do not produce good froths, the froth breaks more quickly than when alkalies are not used; or, this

observation may be used to support the view that the bubbles are better oiled in an alkaline pulp. A froth is also stabilized by the slime present in a pulp, or by other colloidal matter. Colloidal material dissolved in the oils will make an oil-froth more lasting. A mixture of oils, the same as an aqueous solution, gives a better froth than a pure oil.

Considerable weight has been placed by many upon the electro-static forces that might be present in the flotation process. Some have even considered the attraction that holds the sulphide to the bubble-surface to be of this origin. Air bubbled through water has been found to carry ions,[17] and from this, and the fact that most substances have a contact-difference of potential when in contact with water or solutions, an electrical theory has been built up, though in many cases serious errors have been made regarding the action of these forces. Measurements were made to determine these forces. The small metal Callow cell used was grounded, as this condition prevails in actual practice. The charge carried by the air issuing from the flotation pulp was discharged on a metal screen placed above the cell, and the effect measured by means of a Dolezalek electrometer. The readings in this case are measured in volts per minute. The charge upon the air from several pulps was measured and in no case did it exceed 0.011 v. per minute, and was usually only about half that value. The air was negative in neutral pulps, but slightly positive in one of the alkaline pulps. The charge on the froth was also measured, and this varied from zero to 0.011 v. as the maximum. This was sometimes positive, and under other conditions negative. In two good floating pulps the froth was at almost zero potential, though 0.002 v. could easily be determined. It seems, then, that these electro-static effects are far too small to exert any important part in flotation, and cannot possibly be the force that holds the sulphide to the bubble. This, too, would require a dielectric film, such as oil, between the two oppositely charged bodies, the sulphide and the gaseous ions in the bubble; but, since flotation results without the use of oil in many cases,

[17] Lord Kelvin, McLean, and Galt, Proc. Roy. Soc., 1894, 57; Cohen and Mozer, *Ann. Physik.*, 43 (1914) 1048.

and, without doubt, the bubble-surfaces are often not completely covered by oil even when oil is used, it seems that this theory cannot hold. The contact difference of potential of various minerals has been used in some theories. These were also measured by an electro-endosmose method as described by Perrin.[18] To this apparatus a small calibrated tube was sealed at the top of the diaphragm side, so that when dilute electrolytes are used the gas generated can be forced over into this tube, after the experiment is over, and this correction applied to the amount of liquid apparently transferred through the powdered material. The distance between the electrodes was 12 cm. and the potential 110 v. The results obtained give the sign of the charge on the solid in contact with the water or solution, but quantitative results as to the actual potential differences are difficult to obtain in this way. However, some idea can be had by comparing the amount of liquid transferred for the minerals, to that transferred in the case of silica, whose potential difference against water has been found by cataphoresis measurements. This is found to be approximately −0.042 v. For quartz and ferric hydroxide, see Whitney and Blake.[19] The results obtained are as follows:

Mineral.	Liquid.	Sign of Solid.	Liquid Transferred, Cu. mm. per Min.
Silica	Water	Negative	30.7
Alumina	$N/100$ HCl	Positive	40.0
Chalcopyrite	Water	?	Approx. 0
Galena	Water	Negative	3.6
Sphalerite	Water	Negative	6.1
Molybdenite	Water	Negative	3.7
Malachite	Water	Positive	4.0
Malachite	$N/100$ HCl	Positive	17.8
Galena	F. W./500 $FeCl_3$	Positive	44.3

Here the sulphides tested are seen to be slightly negative against water, or practically zero in the case of chalcopyrite. This agrees with our ideas concerning the contact-difference of

[18] *Jour. Chem. Phys.*, 2 (1904), 601.
[19] *Jour. Am. Chem. Soc.*, 26 (1914), 1339.

potential of these substances and with cataphoresis experiments on colloidal sulphides, and the like. Malachite is positive, as would be expected from its basic character. The last result given in the table is probably due to the formation, by hydrolysis, of ferric hydroxide, and its adsorption on the surface of the mineral, so that the action is exactly the same as for ferric hydroxide itself. In this case again, no attraction can exist on the basis of electrical charges between sulphides and oil in emulsions, since they are of the same sign. The charges on oil in emulsions in dilute salt-solutions, etc., are given by Ellis,[20] Powis,[21] and others. This, however, would not determine the charges on a mineral and oil, if the two were in actual contact, as is necessary for flotation. The charges carried by the oil in emulsions are important probably in connection with positively charged colloids which act as poisons, and, of course, the coagulation of slime, and the breaking of an emulsion by electrolytes, is a function of the charge carried by them; but it is not possible to use these charges as an explanation of the primary principles involved in flotation.

The following is a summary of the conclusions arrived at as a result of the experiments made:

(1) For an ore particle to float, it must be interfacial between oil and water, or it must go completely into the oil phase. If no oil be used, the particle must be interfacial between water and air. The force holding the particle to the bubble is much greater when oil is used.

(2) In addition to its value as a lifting agent, the bubble serves to produce a large air-surface in contact with the pulp. This surface is covered to a greater or less extent by an oil-film, to which the mineral may go, so that a small amount of oil is very efficient.

(3) The oil should not be so well emulsified that it will not be given up to the bubble-surface; and yet should be sufficiently emulsified, in a pneumatic process, to last during the time of floating.

(4) Colloids in general are harmful, owing either to their

[20] *Zeit. Phys. Chem.*, 78 (1911), 325.
[21] *Ibid.*, 89 (1914), 91.

causing too stable an emulsion, or to their adsorption on the oil-film at the bubble-surface, preventing mineral attachment. This is the action of the so-called " flotation poisons."

(5) The froth formed is attributable either to the soluble portion of the flotation mixture, which produces a variable surface-tension, or to finely divided or colloidal materials.

(6) Acids, alkalies, and salts affect all these factors.

(7) The electrical effects, other than the colloidal charges, are not important in flotation.

(8) The nature of the solid-surface, in relation to its wetting properties, has been discussed and an explanation of the " hysteresis " of the contact-angle advanced.

In the light of present knowledge it is impossible to measure many of the forces operative in flotation, such, for example, as the interfacial tensions between solids and liquids, or to explain the mechanism of adhesion. Such problems are, however, nearer solution, due to the material advances made recently by Laue,[22] and by Bragg and Bragg,[23] by which the actual arrangement of the atoms in a crystal may be determined, and also by Langmuir,[24] whose work on the constitution of solids and liquids, the structure of solid-surfaces, and the mechanism of adsorption leads toward an understanding of these obscure phenomena.

[22] *Sitz. Akad. Wiss.*, Wien, June, 1912.

[23] *Proc. Camb. Phil. Soc.*, 17 (1912), 43; and treatise on "X-Rays and Crystal Structure."

[24] *Jour. Am. Chem. Soc.*, 38 (1916), 2221.

COLLOIDS

By E. E. Free

The following article is made up of portions of a series of articles on "Colloids in Ore-Dressing," which appeared in the *Engineering and Mining Journal* during 1916.[1] It is a pleasure to express my thanks to the editor of that journal for permission to use the material in this place. The alterations from the original text are almost entirely by way of condensation.

The conceptions of colloids to be found in the current literature of ore-dressing are surprisingly hazy. With increasing interest in the flotation processes the catchwords of two years ago have given way to a new set of phrases involving "surface forces," "interfacial tensions," and the like. The relief to the overworked "colloids" is considerable and one is grateful for the lessened tendency to "explain" obscure phenomena by reference to mysterious "colloidal substances" that, themselves remaining unknown, leave the problem precisely where it was before. This lessened misuse of colloidal concepts appears to be accompanied—one may hope that it is caused—by a more definite appreciation of the physical and chemical nature of colloidal bodies, an appreciation that may be expected to bring important returns in actual experimentation, advancing our knowledge of these bodies and of their metallurgical significance.

In the original text of these papers considerable attention was devoted to the loose use of colloidal terminology caused by a comparison between the kinds of colloids present in ore-slimes and the glue-like bodies, also called "colloids," of which gelatine and albumen are typical. It was pointed out that there are important

[1] *Eng. & Min. Jour.*, Vol. 101, pp. 249–254, 429–432, 509–513, 681–686, 1068–1070, 1105–1108 (February to June, 1916).

differences between these glue-like bodies and the materials encountered in metallurgical practice and that the examination of the latter is best approached by abandoning all preconceptions concerning the gelatinous colloids and by confining attention, in the beginning at least, to the properties of simple rock-powders. So far as is actually known ore-slimes consist merely of fine mineral particles suspended in water that usually contains dissolved traces of the minerals present in the ore. It was asserted that the determinable properties of such a simple suspension of rock-particles in water would explain the behavior of slimes, even the most colloidal ones, without need of assuming the presence of gelatinous substances or other intangible mysteries. It is obvious that the physical properties of simple suspensions become of much importance to the inquiry.

Fortunately, suspensions have been studied thoroughly by geologists, soil-physicists, and the specialists in colloids. The most weighty result of this study is the conception of the possible existence of suspensions of smaller and smaller particles.[2] It is possible to prepare suspensions of clay or other minerals the particles of which are so fine that they remain permanently suspended, though still distinguishable by microscopic examination. It is a small step from this to the typical colloidal solutions that appear free of particles (" optically empty ") before the microscope. The investigations of colloidal solutions made possible by the ultramicroscope,[3] during the past decade, have established firmly the conclusion that the typical colloidal solution, as, for instance, that of colloidal gold, is simply a suspension in which the particles are extraordinarily small.

The important concept here is the perfect continuity of the suspension series. There is no natural break or division of any kind between a suspension of coarse gold fragments in water and a colloidal solution of gold particles so fine as to remain per-

[2] For details see Ashley, U. S. Geological Survey, Bull. 388 (1909) and Bureau of Standards, Technologic Paper 23 (1911), and the general works cited in the appended bibliography.

[3] Siedentopf & Zsigmondy, *Ann. Physik*, Ser. 4, Vol. 10, pp. 1–39 (1903). In English see Zsigmondy, "Colloids and the Ultramicroscope," translated by Alexander, 1909.

manently suspended and be microscopically invisible. It is possible to prepare a suspension of any intermediate degree of fineness. Indeed, if one regards ordinary solutions as composed of single molecules or ions distributed through the mass of the solvent, these " true " solutions appear simply as the limiting case of the suspension series—suspensions in which the particles have become so small as to reach the dimensions of the molecule or the ion.

The immediately obvious objection to this concept of the unity of the suspension series from the coarse visible suspension at one end to the true solution at the other, is that the properties of the systems differ markedly in different parts of the series. A mixture of coarse gold particles and water is very different physically from a colloidal gold solution, and both differ in properties from a solution of, say, gold chloride containing the gold ion. This is quite true, but close examination of the series shows that all differences are of degree only. Thus, in a coarse-sand suspension, the most evident controlling factor is gravity. Nothing but the continuous expenditure of energy (for example by shaking) will keep the sand suspended. As we consider suspensions of finer particles, gravity grows less and less important, while simultaneously the surficial forces between the particles and the aqueous medium grow more and more important until gravity yields control to these other forces and the particles remain in permanent suspension without external assistance. This is typical. The changes are always gradual as one passes up or down the series; they always result from continuous increases or decreases in the intensity of the affecting factors. They are never abrupt. From the practical viewpoint, however, it is precisely these gradual changes of degree that are important. The fact that the properties of the finer-grained suspensions do differ from those of the coarser is what has attracted attention. It is important theoretically to know that the differences are of degree rather than kind, but that does not dispose of the differences.

The most troublesome properties of colloidal ores are two, namely, the slow settling of slime, which also means the imperfect separation between fine and coarse particles, and the low perme-

ability of settled masses of slime, filter-cakes, and the like. The latter is usually accompanied by a high retention of water in the thickened slimes. Both of these are comparative rather than absolute. The colloidal slime settles slowly and packs imperviously by comparison with slime that is less colloidal. It is easy to demonstrate by experiment with suspensions of known character that slowness of settling and the other troublesome properties increase gradually and continuously with decrease of the particle, and it is an obvious inference that an unusually small size of particle is the cause of all the trouble with colloidal slimes. The mechanisms may be pictured by recalling that in dilute suspensions gravity becomes less important and surficial forces more important as the particles decrease in size, and that in thickened masses of slime, if the particles are very small, the spaces between the particles are similarly tiny and offer tremendous frictional resistance to the percolation of water.

These effects of minute particles are so manifest and so manifestly sufficient to explain the behavior of slime that I suspect no other explanation would have been suggested were it not for the anomalous fact that the degree of colloidality of a slime has no constant or determinable relation to the fineness of grinding of the ore or to the amount of very fine material in the slime as determined by screen-tests, by elutriation, or by other methods. There is much more likely to be a relation to the original character of the ore. For instance, oxidized and " rotten " ores are especially prone to yield colloidal slimes. These anomalies are to be explained by two things: the variable disintegration of ores and the variable flocculation of the slimes. The ease of disintegration is essentially a matter of mineral composition. Mechanical grinding by itself cannot reduce ore-particles beyond a certain size, which is probably considerably above the size necessary for high colloidality. If disintegration occurs beyond this limit of mechanical grinding it is because the ore or some of its constituents are of such physical nature as to disintegrate spontaneously when shaken with water, as, for instance, clay will disintegrate. Natural processes of weathering in the oxidation zone tend to produce materials that will so disintegrate, as, for instance, when

feldspar is altered to kaolin. By the second factor, flocculation, is meant the aggregation of several smaller particles into more or less persistent groups or floccules, which then behave much like single larger particles. This will be discussed in detail below.

The most important result of the study of colloids and suspensions during the past decade is the conception of colloids simply as suspensions the particles of which are very small.[4] It is unnecessary to make any sharp distinction between suspensions and colloidal solutions. The emphasis, indeed, is reversed and is on the unity of this series rather than on any possible severalty; but for the purposes of purer science it is convenient to have distinctions, so that a greater precision of definition becomes necessary. For these purposes there has come to be nearly general agreement on a set of size-limits given in the following table:[5]

CLASSIFICATION BY SIZE OF PARTICLES

Suspensions	Particles over 0.1 micron in mean diameter
Colloidal solutions	Particles between 0.1 and 0.001 micron in mean diameter
True solutions	Particles under 0.001 micron in mean diameter

While these limits are purely arbitrary, the use of them is convenient as indicating the range of size within which the typical colloidal properties are best developed. It is not implied that these properties cease entirely to be exhibited by suspensions the particles of which lie outside these limits. In metallurgy especially it is necessary to consider many important extensions of colloidal properties into the field of the coarser suspensions. Nearly all slimes, even the most colloidal, belong to the field of suspensions rather than to that of colloidal solutions, as these fields are defined by the size-limits given.

[4] The detailed experimental evidence supporting this conclusion is ample and beyond question, but its discussion would require too much space. It will be found in detail in the works of Freundlich, Ostwald, and Zsigmondy, cited in the appended bibliography. It is excellently summarized by John Johnstone in his introduction to Ashley's monograph on the "Technical Control of the Colloidal Matter of Clays," U. S. Bureau of Standards, Technologic Paper 23 (1913).

[5] Zsigmondy, "Erkenntniss der Kolloide," p. 22 (1905). A micron is one-thousandth of a millimetre, or approximately one twenty-thousandth of an inch.

This conception of colloids points immediately at the chief characteristic of these bodies and the one that is at the bottom of most of their properties, namely, their great internal surface. It is manifest that if a colloid is composed of very fine particles of one substance suspended in another, the total surface of contact between the two substances will be very great. This mutual surface is called the internal surface. It has been found that a number of peculiar properties, of which surface-tension is the best-known, characterize all surfaces where two substances come into contact, and the great extent of such surface in suspensions and colloids gives these surficial properties and forces an unusual importance in controlling the salient characteristics of the entire system. For instance, the phenomena of adsorption or the concentration of dissolved substances at surfaces are exhibited in a high degree by suspensions and colloids and are of much technical importance in dyeing, the clarification of wines, the manufacture of contact sulphuric acid, and in many other industrial processes.

In speaking of the large internal surface of colloids one means, of course, that the surface is relatively extensive with respect to the masses involved. The criterion is a large ratio of internal surface to mass. Formal definitions are of small value, but it is possible to define a colloid from this viewpoint as a mixture of at least two substances the internal surface of which is very large relative to the mass of at least one of the substances. It may be pointed out again that the definition is purely relative. What ratio of surface to mass is to be considered " very large " will depend upon circumstances.

In the foregoing paragraphs there has been much mention of colloidal properties, but the only ones that have been discussed specifically are the slow settling of colloidal slimes and their imperviousness when settled. From the standpoint of ore-dressing these two are the most important of all colloidal properties, and the emphasis is not unjustified. However, several other properties are of interest. Most important scientifically are the similarities to, and differences from, the true or ordinary solutions the particles of which are supposed to be of molecular or ionic dimen-

sions. The typical colloidal solution resembles a true solution in being persistent so long as conditions remain unchanged. That is, the particles remain in suspension and the colloidal solution retains an unchanged chemical composition. The colloids differ in (1) failure to show a true and constant solubility; (2) an optical heterogeneity shown by translucence or turbidity; (3) the causing of no change, or a very small change, in the freezing-point and boiling-point of the solvent; (4) the production of no osmotic pressure; (5) slow diffusion and failure to dialyze or pass through a parchment membrane. The causes of all these differences will be evident on consideration of the difference in particle-size that distinguishes the colloids from the true solutions. Details need not be pursued further than to say that the differences, as before, are of degree only. Colloids do not fail entirely to show the typical solution properties, but they show them to so slight a degree as to escape all but the most painstaking researches.

Of the other properties of colloids, flocculation and adsorption have been mentioned and will be discussed further below. Another, of much technical importance, is the tendency of the colloidal particles to wander in the electric field and accumulate at one or the other of the poles. This forms the basis of the well-known Cottrell process for the collection of acid and smelter-fume, the removal of dust from stack-gases, the separation of oil-globules from condenser-water, and the like.

In what precedes, the reader has probably detected a tacit assumption that all colloids consist of solid particles suspended in a liquid medium. It is easiest to attain an initial concept of the nature of colloids by regarding them in this way, but the concept is incomplete. Common experience furnishes numerous examples outside this simple case. For instance, the usual medicinal emulsions of cod-liver oil, or, to use an illustration with pleasanter associations, the ordinary oil-vinegar salad dressing, consists of globules of oil suspended in an aqueous liquid. Obviously both particle and medium are liquid, yet the properties of the mixture are (with some exceptions in detail) the typical colloidal properties. As a matter of fact it is possible to prepare

of particle or a medium that is itself complex, and it is not necessary for all of the particles to be solid, or liquid, or of any single state.

The particulate theory of colloids and the classification according to the respective physical states of the phases is reflected in the terminology developed for the subject. Thus a useful concept regards the size of particle as due to the " degree of dispersion " of the particulate substance. A decreased size of particle is spoken of as a greater " dispersion," or the substance as more highly " dispersed." By extension all suspensions and colloids are " disperse " (or " dispersed ") systems or " dispersoids "; the particles compose the " disperse " phase and the medium is the " dispersion medium." A true solution possesses a molecular or ionic degree of dispersion and is a " mol " or " ion-dispersoid." [7] These terms include all colloidal systems, regardless of the solid, liquid, or gaseous state of particle or medium. Colloidal solutions with a liquid medium are referred to as " sols." If the medium is water, the colloid is a " hydrosol "; if alcohol, an " alcoholsol," or " alcosol," etc. By analogy with the systems of coarser particles the solid-particle sols are frequently called " suspensoids "; those of liquid particles, " emulsoids." The terms " sol," " suspensoid," and " emulsoid," with their compounds, are properly applied only to systems within the assigned colloidal range of particle size.

The distinction between emulsoids and suspensoids on the basis of the liquid or solid character of suspended particles has been generally accepted, but recent evidence indicates that this is not precisely the ground of difference between typical members of the two classes. The typical emulsoids are gelatine and the related glue-like colloids. The typical suspensoids are the colloidal solutions of metals. These classes differ markedly in many properties; for instance, the metal sols are much more easily precipitated by electrolytes. However, a suspension of small droplets of mineral-oil in water behaves much more like the

[7] This terminology is due to Wo. Ostwald, *Koll. Zeits.*, Vol. I., pp. 291–300, 331–41 (1907); "Grundriss der Kolloidchemie," first ed., p. 83 (1909); English ed., p. 24.

metal sols than like the typical emulsoids such as gelatine. It is probable that the explanation lies in two facts. First, the globules of oil are so small that they are practically rigid and behave like solid particles. Second, the materials of the typical glue-like emulsoids are miscible with water. Thus the gelatine sol has been shown to consist of two phases both of which are solutions of gelatine in water.[8] The globules are composed of a concentrated solution of gelatine and are in a medium that is a dilute solution of gelatine. Under proper circumstances water can pass from globule to medium or the reverse, resulting in changes of the gelatine concentrations in the two phases and in shrinkage or swelling of the globule phase. It is believed that this behavior is responsible for the peculiar properties of the glue-like colloids and it is probable that we must recognize two classes of emulsoids, as that term is above defined. One class will consist of those liquid-particle colloids the particles of which cannot absorb the medium, like, for instance, mineral-oil in water. The other class will contain those in which water can be absorbed by the particle. These will include gelatine and its analogues.

It is the emulsoids of this second class that form the " gels " ; jellies of the sort typified by the ordinary table jellies made from gelatine or the pectin of fruit-juices. The discussion of the structure and properties of gels would take us far afield. It may be noted, however, that the only inorganic gel of common occurrence is that of silicic acid or hydrated silica. The effect of the gel-forming emulsoids on the flocculation of suspensions will be noted below and we shall then return briefly to the possibility of their occurrence in ores and slimes.

From the practical point of view, in ore-dressing at least, the most important properties of colloids and other suspensions are those that are concerned with the rate of subsidence of the particles through the medium. This is what controls the rate of settling of slimes and the many practical matters depending thereon. When a single mineral particle falls freely through water or any fluid medium it soon attains (if it be not too large) a constant

[8] Hatschek, "Introduction to the Physics and Chemistry of Colloids," p. 46 (1913).

velocity, which is maintained thereafter regardless of the distance it falls. This constant velocity is expressed mathematically by a formula due to Stokes,[9] as follows:

$$v = \frac{2}{9k} r^2 (d - d^1) g$$

in which v is the velocity, r is the radius of the particle, d and d^1 are the densities of the particle and medium respectively, g is the acceleration of gravity, and k is a constant depending upon the viscosity of the solution.

Ignoring the self-evident effects of gravity and of the difference in densities, it is apparent that the velocity of fall of a particle will vary directly with the square of its radius and inversely with the viscosity of the medium through which it falls. The chief departures from this formula that are encountered in experiment occur with the smaller particles, these falling more slowly than is required by the theory. It is probable that such deviations are due to several forces, active only in the case of the finer particles and not taken into account in the formula, of which forces the chief appear to be molecular bombardment and electric charges on the particles. The possible efficacy of repulsive electric charges in modifying the rate of fall is obvious. Knowledge of the importance of molecular bombardment is due to recent work demonstrating that the vibratory movement of suspended particles, known as the Brownian movement, is really due to bombardment of the particles by the moving molecules of, or in, the medium.[10] It follows that small suspended particles have in some degree a tendency to become distributed throughout the medium, a tendency similar in kind to the diffusiveness of a gas or of a dissolved substance, but much less intense. In actual experiment, furthermore, we seldom deal with a medium entirely free from convection currents and even less often with particles

[9] Trans. Camb. Phil. Soc., Vol. 9, Part 2, pp. 51–52 (1850). For more recent treatments see Cunningham, Proc. Roy. Soc. (London), Ser. A, Vol. 83, pp. 357–65 (1910) and Lamb, *Phil. Mag.*, Ser. 6, Vol. 21, pp. 112–21 (1911).

[10] For a review of this subject, with citations of literature see Wo. Ostwald, "Grundriss der Kolloidchemie," 2d ed., pp. 231–61 (1911); English ed. pp. 186–210.

that are perfect spheres. Any such disturbances in the medium or irregularities in shape of the particle will retard settling, and it is obvious that the rates of fall actually found may be importantly below those expected on the basis of the formula. All of these disturbing factors lead to decreases rather than increases in the rate of settling required by the formula, which it is possible to regard as an expression of the limiting maximum velocity that a given particle can attain in a given medium. The actual velocity will be always smaller than the theoretical.

From the presence in the formula of the square of the radius of the particle it follows that the velocity of fall decreases rapidly with decrease in size. In this and in the fact that all deviations are toward lesser rather than greater rates lies the cause of the extremely slow rates of subsidence exhibited by fine clays, slimes, and the like. Indeed, with ordinary mineral particles in an aqueous medium and under the usual conditions of experiment or of metallurgical practice, single particles entirely cease to subside, although large enough to be microscopically visible and considerably larger than the diameter established by the Zsigmondy table as the upper limit of truly colloidal particles. This means that suspensions that are not fine-grained enough to be colloids at all, in the technical sense of the word, are capable of persistent suspension and that much of the material of many slimes would not settle at all were it controlled only by the factors mentioned. The fact that slimes do settle and that the situation is not so bad as would be inferred from the theory outlined brings us to the matter of flocculation.

Flocculation is the technical term for the gathering of suspended particles into aggregates. An aggregate composed of many particles will behave to some degree like a single larger particle, although one of very irregular surface. It follows that flocculation changes the suspension from one of a multitude of tiny particles into one that behaves as though it were composed of a relatively small number of larger particles. The average effective radius of particle is increased, and the Stokes formula indicates the increase to be expected in the rate of settling, it being remembered that this increase will correspond to the squares

of the respective radii. Experiment is fully confirmatory. A flocculated clay-suspension will subside in a few minutes whereas the same material, unflocculated, may remain suspended indefinitely. The rate of settling may be largely increased, even multiplied by hundreds or thousands, by flocculation, and in this lies the explanation of much of the anomalous behavior of colloidal slimes. Slimes settle faster or more slowly not only in response to the actual size of the ultimate mineral particles, but also in response to the more or less complete flocculation of these ultimate particles into larger or smaller aggregates. These floccules are not fixed enough to persist through screen-testing or elutriation even when it can be carried to their dimensions, and the reason for the failure of such tests to agree with the degree of colloidality encountered in practice is clear.

It should be noted that flocculation and its opposite, deflocculation, are purely relative terms like, for instance, "high" and "low" or "smoothness" and "roughness." A suspension is more or less flocculated merely with reference to some other suspension. For this reason it is preferable to use the concept of "degree of flocculation" rather than to refer to suspensions as "flocculated" or "deflocculated." Precision in the determination of this degree of flocculation is not yet possible. No method is known for the accurate measurement of floccules or the counting of their constituent particles, and even if there were, it is probable that the individual floccules of a single suspension would vary widely and irregularly among themselves.

The degree of flocculation of a suspension is extremely sensitive to surrounding conditions; so sensitive, indeed, that changes of flocculation in the true colloidal solutions are among the most delicate of analytical reactions. These changes and similar ones in the coarser suspensions may be caused by many kinds of influences. Temperature, light, the radiations from radium, electro-static charges, and many other variations in energy relations all appear to have perceptible effects. However, these effects of direct energy are less important than the effects of added substances, and it is these latter alone that require consideration here. A large amount of observation and incidental

experiment going back for centuries has established three general classes of substances that affect the degree of flocculation or, as it is generally conceived, the rate of settling of suspensions. First are the neutral inorganic salts and the inorganic acids, all of which increase the degree of flocculation and promote settling. Second are the alkalies which (in certain concentrations) have the reverse effect; they decrease the degree of flocculation and hinder settling. These are known as "deflocculators." Third are the gel-forming emulsoids, such as gelatine and the like. The

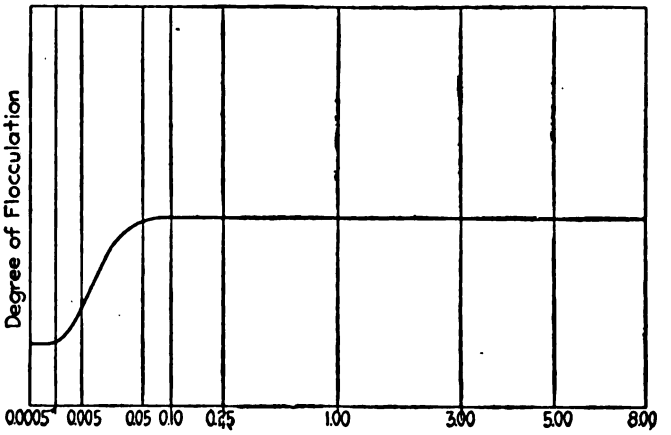


FIG. 1.

effect of these is somewhat complex, but in general they also decrease the degree of flocculation, or at least prevent its increase.

A convenient illustration of the effect of a flocculating agent is furnished by a series of measurements of the flocculating effect of sodium chloride upon kaolin suspensions recently made by Herbert F. McCall under my direction. The data are shown graphically in Fig. 1, the degree of flocculation being expressed upon the vertical axis, the concentration of sodium chloride upon the horizontal. For convenience the scale of the horizontal axis is cubed. The degree of flocculation cannot be set down in any absolute or standard units. The curve expresses no more than the relative degree of flocculation of suspensions in solutions of different concentration and has, so far as its vertical di-

mension is concerned, only a roughly quantitative value. From this curve it is apparent that in extremely dilute solutions there is no perceptible effect on the degree of flocculation. At a concentration of about 0.0005 gram per litre an increased flocculation begins to be perceptible; this increases rather rapidly at first and then more slowly to a maximum at about 0.07 gm. per litre, beyond which increases of concentration produce no further perceptible effect on the degree of flocculation. The experiments were extended to saturation (250 gm. per litre), but the corresponding portion of the curve is not shown in the figure.

This behavior is characteristic of nearly all soluble salts and acids acting on most suspended substances. The initial concentration at which an effect begins to be apparent is known as the "threshold concentration," and varies considerably in suspensions of different materials and with different salts or acids. It is worth noting that, contrary to the current conception of the matter, this threshold concentration is not a sharp point at which the flocculation begins suddenly—like, for instance, the beginning of boiling at a definite temperature—but is rather a range of concentrations inside which the flocculating effect begins and rises more or less gradually to its maximum.

The different acids and salts vary greatly in flocculating power, but these variations have not been investigated with precision. Among typical colloids such as colloidal metals there are many cases in which the flocculating action of added salts appears to increase rapidly with rise in the valence of the flocculating ion. The salts of univalent elements are least active, those of bivalent elements somewhat more active, those of the trivalent elements still more active, and so on. However, there are many exceptions and general application of the rule is not possible. Doubtless further investigation will supply principles for the prediction of the flocculating powers of various salts, but at present these powers must be regarded as individual and specific.

In solutions of the alkalies the relations are more complex. Fig. 2 gives the effect of potassium hydroxide on the degree of

flocculation of kaolin suspensions as determined by F. K. Cameron and Free.[11] It is apparent that the degree of flocculation in pure water is not zero, but is importantly greater than in some of the alkaline solutions.

There is again the phenomenon of the threshold concentration, but when the threshold is passed, the effect is a decrease rather than an increase in the degree of flocculation and there is a zone of deflocculation reaching to a concentration of nearly 1 gram per litre. As concentration increases beyond this, there is an increased flocculation, surpassing at about 4 gm. per

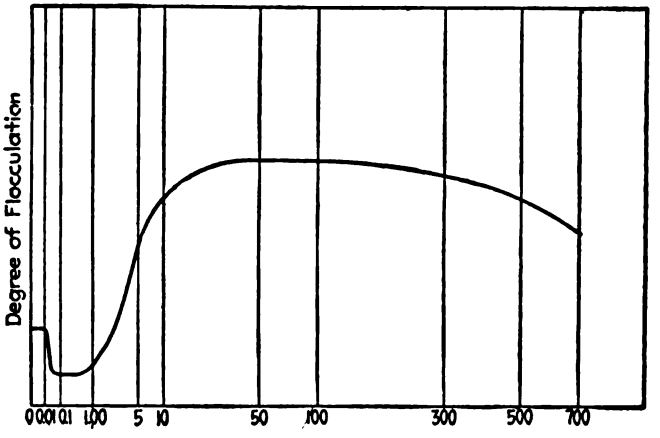


FIG. 2.

litre the degree of flocculation attained in pure water and rising thenceforth to a maximum of flocculation at about 30 gm. per litre. In greater concentrations there is a decrease, which, however, may be in part merely apparent and due to increasing viscosity and density of the solutions. The characteristic deflocculating effect of alkali appears to be an effect over a certain concentration range only. At higher concentrations there is a flocculating effect not unlike that of the acids and neutral salts.

Concerning the effect of the remaining class of deflocculators, the organic colloids, there is, paradoxically, rather less of precise

[11] Cameron and Free, *Science* (n.s.), Vol. 32, p. 482 (1910); Free, Jour. Frank. Inst., Vol. 169, pp. 430–4 (1910).

experimentation but more of theoretical understanding. Substances of this class tend to prevent the flocculation that normally exists or that would otherwise occur on the addition of flocculating agents. It is matter of common knowledge that glue, gelatine, and the like will prevent the subsidence of suspensions, and the similar effects on plastic clays have long found commercial employment. It is significant that these deflocculating effects are exhibited only by colloids composed of liquid particles. It has been suggested that the protective action is due to the coalescence of the liquid droplets of the colloid with the particles of the suspension that it is stabilizing. In this manner liquid films of the protective colloid are formed about the particles of the suspension, and the resultant change in surficial properties is supposed to be responsible for the failure of these particles to flocculate and subside. There is much evidence favorable to this conception of the mechanism and it is generally accepted.

It is important to note that most mineral powders, including all ordinary slimes, exhibit a considerable degree of flocculation when they are suspended in water even when no flocculating agent has been added. It does not matter whether this normal flocculation be regarded as a property of the pure mineral in pure water or considered an effect of the traces of flocculating substances (for instance, carbon di-oxide) present in ordinary waters. The significant fact is that normal slime is always more or less flocculated. Excessive colloidality is usually due to the presence of some substance or circumstance that acts as a deflocculator and destroys or prevents such flocculation as would otherwise occur. It becomes important, therefore, to search out the cause or causes responsible for this deflocculation. It is natural to think of alkalies or of organic colloids, both of which are known to be deflocculators. Traces of alkali in ores are not impossible, especially in highly weathered ores, which are most subject to colloidal difficulties. That the alkali can reach ordinarily a concentration sufficient to develop the deflocculating effect is less probable. The glue-like colloids are not to be expected in slimes except in those rare cases in which slime or mill-water has become contaminated with decaying vegetation or

other organic material. If excessive colloidality in general is due in any degree to the deflocculating action of emulsoid colloids it must be because of the presence of some inorganic emulsoid and the only such emulsoid now known and at all probable in rock-powders is colloidal silicic acid. This substance has never been identified in slime but it is possible that it is produced superficially on particles of silicate minerals by the action of water or water containing dissolved carbon di-oxide. Cushman[12] has observed surface alterations of silicate fragments after long grinding with water, and these alterations may correspond to something of this kind. It is difficult to see how any such alterations could occur on sulphide particles or any minerals other than silicates, but the entire matter of deflocculation in slime is so little known that speculation is of small value. Detailed experimentation is essential to a better understanding of the matter and this experimentation may disclose active causes now entirely unsuspected.

Aside from the matter of removing the cause of excessive deflocculation, if that cause can be discovered, there is a possibility of increasing the degree of flocculation by the addition of flocculating salts or acids, as suggested especially by Ashley.[13] From the curve of Fig. 1 it is apparent that the minimum active concentration (the threshold concentration) of sodium chloride is not high, and this is true of most of the flocculating salts. There is nothing inherently impracticable in the use of such flocculating agents in ore-dressing; this is already done in several industries and is a common procedure in slime-testing, and in the analytical laboratory generally. An important series of experiments on the action of flocculating agents on slimes has recently been reported by Ralston.[14] Other experiments (with common salt and with ferrous sulphate) have been reported by Laist and Wiggin,[15] whereas Caldecott [16] has observed in practice the reverse,

[12] U. S. Department of Agriculture, Bureau of Chemistry, Bull. 92, 24 pp. (1905).

[13] Trans. A. I. M. E., Vol. 41, pp. 380–95 (1910).

[14] *Eng. & Min. Jour.*, Vol. 101, pp. 763–769, 890–894, 990–994 (1916).

[15] Bull. A. I. M. E., No. 92, pp. 2201–16 (1914).

[16] Proc. Chem. Met. Soc., S. A., Vol. 2, pp. 381–429 (1898).

or deflocculating, effect of caustic soda. In this connection it should be noted that the acid or other solutions used in the several leaching processes, and probably also the usual cyanide solutions, have a flocculating action that is not unimportant, although the employment of these solutions is for other ends.

A word must be devoted to the use of lime as a flocculating agent, this material having been used by a number of engineers.[17] At first sight it would appear improbable that lime could have a purely physical flocculating action, lime being an alkali and the characteristic effect of small concentrations of alkali appearing to be a deflocculation rather than the reverse. There is nevertheless a certain flocculating action exhibited by lime, even under laboratory conditions, and it appears that the hydroxides of calcium, and probably of magnesium, do not behave exactly like potassium and sodium hydroxides. It appears probable, also, that certain purely chemical factors enter as well and that the efficacy of lime as a clarifier is due in part to chemical reactions of the same sort as those that control, for instance, the action of aluminum salts in clarifying water. These clarifying actions apparently depend upon the formation by chemical reaction of some flocculent precipitate that entangles and sweeps down the suspended particles. Probably the occasional cases of clarification by organic colloids [18] belong to the same class.

The preceding discussion of the causes of excessive colloidality of slime may be summarized as follows. The necessary conditions for the production of a colloidal slime are two: (1) great fineness of particle of at least a part of the slime; (2) a low degree of flocculation of this finely-divided material. Both conditions are necessary. Neither is sufficient alone. It is useless to enter here into the question of fineness of particle or its possible control. Usually such a degree of control as might entirely prevent the production of a very fine material is not practicable, and no less degree of control will be of much assistance against colloidal troubles. The degree of flocculation will be increased

[17] See, for instance, Richards, "Ore Dressing," Vol. 2, p. 1149, and Vol. 3, pp. 1416–17 (1903 and 1909).

[18] See Ralston, *loc. cit.*

by dissolved salts and acids in practically all concentrations and by alkalies in certain concentrations, mostly high. It will be decreased by low concentrations of some alkalies and by the presence of organic gelatinous coatings, in the rare cases when these are present. It is possible that surface alteration of silicate particles, or some other cause, may produce colloidal silicic acid, which may then act as an emulsoid deflocculator. If this is due to surface alteration of the particles it will probably be favored by long-continued grinding or by storage in contact with water, especially in the presence of carbon di-oxide, as, for instance, under long exposure to the atmosphere. High temperatures also favor this alteration. There are probably many other factors affecting the degree of flocculation but they remain unknown.

Ignoring minor uncertainties and assuming a slime of constant fineness, rules for practical procedure may be stated thus: colloidality will be increased by (1) the presence of small amounts of free alkali (except lime), (2) prolonged grinding or long exposure to water or the atmosphere, (3) grinding or storage at high temperatures, (4) the presence of organic materials such as would be supplied by decaying animal or vegetal matter. Colloidality will be decreased by the avoidance of the four conditions just cited and also by (1) the presence in solution of acids or of neutral salts or of certain alkalies in certain concentrations and (2) rapid grinding and handling. The relative quantitative importance of the various factors mentioned and the decision as to which should be selected as a means of practical improvement will depend upon local conditions different in each case. In general, the presence of organic matter has the most effect, but is rarely encountered. Next in quantitative importance is the presence of dissolved acids, salts, or alkalies. Of much less effect is the time of grinding, or storage unless it runs into years, and of still less effect are changes, between usual limits, in the temperature of grinding or storage.

With the recent remarkable development of flotation processes much interest has been focused on the fact that these processes work much less successfully on " very fine " slime than on

material of larger particles. The failure is frequently ascribed to colloidal difficulties in slimes. It is difficult to discuss this matter usefully. The basic theory of the flotation process is not known and no theory has proved generally satisfactory. Accordingly the following suggestions are offered tentatively and merely as a contribution to the current discussion. Only from the slow progress of experimentation can one expect a dependable theory of the flotation processes or of the relations of colloidal theory to them.

Regardless of ultimate theory it seems evident that the essential thing in the flotation process is the tendency of certain minerals to attach themselves to films or globules of oil or to complexes consisting of oil-globules and air (or gas)-bubbles. This tendency of attachment or adhesion varies with different minerals (as well as with different oils) and thus provides a possibility of mineralogical separations. The various matters of froth production, gravitational separation, generation or incorporation of the air or gas, and the like, are all secondary, from my viewpoint, to the fundamental matter of the differential attachment of minerals to the oil or the oil-gas complex. And so far as the size or mineral nature of the particles is concerned interest may be confined to the attachment between the mineral and the oil. The attachment of gas-bubble and oil-film or the maintenance of whatever kind of oil-gas complex is desired may be important to the success of the process, but it will depend upon the mutual properties of oil and gas and not upon the properties of the mineral particles. These matters can have no direct effect on the attachment between the mineral and the oil. It seems probable, therefore, that answers to questions concerning the inapplicability of flotation to slimes are to be sought in the peculiarities of the forces controlling the oil-mineral attachment.

It is customary to refer to these forces as interfacial tensions. This is merely a matter of words. The fact seems to be that surfaces of contact between dissimilar substances have peculiar properties, which properties are instanced by adsorption and the surface-tension of liquids and which have been referred to above as important among the characteristics of col-

loids. It appears that the surficial layer of atoms in any mass of matter has properties somewhat different from those of atoms within the mass. When two masses of different kinds of atoms are in contact the one kind of atoms may affect the other kind across the surface, and hence the differences in behavior of surficial atoms, which differences constitute the "properties of the surface," may depend upon the natures of *both* the substances in contact. The fundamental theory of these differences in the surficial layers of atoms is unknown but the recent papers of Langmuir [19] are most suggestive.

The special characteristics of surfaces are exhibited, in the main, by two things: adsorption and the surface-tension of liquids. Adsorption has been referred to above as the tendency of dissolved substances to concentrate at the surface of the liquid, either a free surface exposed to the atmosphere or a surface in contact with solids. The best instances are furnished by finely divided solids, which have the great ratio of internal surface to mass mentioned above. Thus, powdered charcoal will remove nearly all of certain dyes from their aqueous solutions by adsorption alone, without chemical reaction or destruction of the dye. Surface-tension is shown in the tendency of liquid globules to take spherical form and, in general, the tendency of all liquid surfaces to contract whenever not prevented by external forces. The liquid may be supposed to draw itself together into the most compact shape possible. Among other peculiarities, both adsorption and surface-tension have the characteristic of varying with the curvature of the surface, especially when the radius of curvature is very small. Thus substances in very fine fragments or droplets have properties significantly different from the properties of the same substances in mass. For instance, the solubilities and vapor-pressures are greater. Here again the mechanism is imperfectly understood, but it is not necessary to the present argument.

Returning to the conditions present in the flotation process, if the essential matter is the establishment and persistence of the

[19] *Met. & Chem. Eng.*, Vol. 15, pp. 468-470 (1916); Jour. Amer. Chem. Soc., Vol. 38, pp. 2221-2295 (1916).

attachment between mineral and oil and if the tendency to this attachment varies, as do adsorption and surface-tension, with the curvature of the active surface, it is evident that the tendency to attachment may vary markedly with the size of the mineral particle. As a particle decreases in size the average radius of curvature becomes very short. Attachment to the oil might be rendered more easy or less easy—one could not decide which, *a priori*—but it would be likely to be affected in some way. A further complication is introduced by the matter of adsorbed films on the mineral particles. These particles do not present to the oil-globules mineral faces fresh from cleavage and therefore clean. The surface actually presented has been in contact with water or air or both, and the water has probably contained many dissolved substances. It follows that the oil must not only attach itself to the mineral surface but, in order to do so, must displace from that surface a film of water, air, or some dissolved material or materials adsorbed from the water with which the particle was previously in contact. It is probable, though I do not think it is certain, that such attached films of water, air, or other adsorbed substances are held more tenaciously when the particles are small than when they are large. If so, it is possible that such adsorbed films might prevent the necessary oil-attachment in slime but not in larger particles.

It is not necessary, of course, that the disturbing effect of small particle-size should operate always or merely to prevent oil-attachment. The flotational separation would be equally impaired if the tendency to oil-attachment were increased, provided that this increase affected the non-metallic minerals as well as the metallic. All that is necessary to destroy the efficacy of the flotation process is that something should impair the differential character of the attachment of oil to different minerals. The argument outlined above will indicate that this is quite to be expected when the mineral particles become unduly small. As particle-size decreases the properties of the surface become more important, those of the mass (for instance, specific gravity) become less so. Small particles tend to behave more and more alike the smaller they are, regardless of the minerals (or other

substances) of which they happen to be composed. Much significant and suggestive work indicates, in general, that surfaces of different substances are much more nearly alike in essential physical properties than are masses of the same substances.

It is not particularly encouraging to come out of the argument merely with the conclusion that the inefficacy of the flotation process with slimes is to be expected. One hoped for suggestion as to how the disability might be removed. It does not seem probable that such suggestions will be forthcoming until the nature of the surface properties of substances shall have been elucidated by further investigation. Improvements made in the meantime in the application of the flotation process to slimes are likely to be purely empirical and largely accidental. Such improvements have been made and undoubtedly will be repeated, but it is to be hoped that detailed investigation of the properties of surfaces will furnish before long a surer ground of progress.

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DIFFERENTIAL FLOTATION

By O. C. Ralston

Introduction.—Many names are used to express the fundamental idea conveyed by the above title. "Preferential" is used more particularly to designate the process claimed in patents issued to E. J. Horwood of Australia. "Differential" implies that one mineral is being floated to a greater degree than another flotative mineral also present. Moreover, it is a broader term than "preferential" because the latter is coming to mean the process, patented by the man who used it first, equivalent to fractional roasting and flotation. "Differential" has found acceptance in England and in Australia but it has not yet been adopted in the United States.

For the benefit of those who have not read my earlier compilation misnamed "Preferential Flotation," [1] it may be well to abstract a portion and to state that differential flotation is now obtainable in three ways:

I. By fractional roasting and flotation.

II. By the use of certain dissolved substances in the pulp.

III. By close control of the physical conditions regulating flotation.

I. **Fractional Roasting.**—H. A. Wentworth, in U. S. patent No. 938,732, of 1909, claimed the fractional roasting of "ore mixtures containing several sulphides," so that one mineral would be deadened while the others would float. He seems to have meant film-flotation.

A. S. Ramage, in U. S. patent No. 949,002 of 1910, stated that the "principle of my process is founded on the combination of fractional roasting with chemical floating"; in other words,

[1] *M. & S. P.*, June 26, 1915, Also "The Flotation Process," by T. A. Rickard, p. 71.

he had particularly in mind the warm-acid methods of De Bavay, Potter, and Delprat.

E. J. Horwood, in U. S. patent No. 1,020,353 of 1912 and No. 1,108,440 of 1914, claims " preferential flotation," which depends on deadening the surfaces of such minerals as galena and pyrite by a short flash-roast, while sphalerite and chalcopyrite are unaffected and can be later removed by flotation. This process [2] has been employed on the Broken Hill mines of the Zinc Corporation and the flotation used has been the modern air-frothing method of the Minerals Separation company.

Fractional roasting and flotation are said to be in use in the North Star mill of the Federal Mining & Smelting Co., near Hailey, Idaho. The most serious objection to it is the large amount of sulphuric acid necessary in order to obtain good flotation of the zinc sulphide after the roasting. The iron sulphides are effectively deadened.

In the mill of the Progress Mining & Milling Co., near Robinson, Colorado, a complex zinc-iron-lead ore is receiving table-treatment to make a good lead concentrate and a zinc-iron middling. This middling is roasted, ground, and treated in a mechanical agitator for flotation of the zinc.

In U. S. patents, 1,197,589 and 1,197,590 of September 12, 1916, Raymond F. Bacon calls attention to the fact that in such fractional-roasting processes part of the minerals that it is desired to have deadened will not be oxidized and part of those that are not wanted to oxidize are nevertheless oxidized. Besides, in some ores the sulphides are so intimately mixed that a clean separation is impossible by any crushing process. He inclines toward more complete oxidation of the ore, followed by sulphidizing with a soluble sulphide, or even getting one of the constituents into solution and then sulphidizing. Thus, for pyritic ores containing some copper, the treatment recommended is to roast long enough to completely decompose the iron sulphides, although part of the chalcopyrite will resist roasting. During the roasting part of the copper minerals will also be

[2] The operation of this process is well described by Allan D. Rain in *M. & S. P.* of Oct. 7, 1916.

roasted and lost if treated directly by most of the previously mentioned methods of fractional roasting and flotation. Bacon treats the fractionally roasted ores with enough sulphuric acid to get the copper into solution and then adds hydrogen sulphide to precipitate it as sulphide. The flotation treatment that follows will then recover both the natural and the artificial sulphides of copper.

In the case of copper-zinc sulphides the same idea can be applied. A complete roasting of the ore is necessary, and then copper and zinc are taken into solution by sulphuric or other acid. The application of hydrogen sulphide to the pulp containing this solution will precipitate only copper sulphide. After flotation of the copper sulphide the pulp is neutralized and an alkaline sulphide is added to precipitate zinc sulphide, which is then likewise floated to remove it from the gangue. In commenting on this process, I would say that in the first place the complete roasting of zinc sulphide is a difficult and expensive operation. Secondly, there would almost certainly be some iron dissolved from the ore and it would accompany the zinc, being precipitated as iron sulphide with the zinc sulphide. This is undesirable from the standpoint of the zinc smelter. Moreover, the flotation of copper sulphide in the presence of large amounts of zinc and iron sulphides in solution presents considerable difficulty. Since Dr. Bacon also claims the application of this method directly to oxidized ores, as well as to the above-mentioned sulphide ores, and as oxidized ores nearly always contain considerable amounts of acid-soluble iron compounds, I am inclined to believe that he has obtained a "paper patent."

Numerous other separations of this kind are claimed in his patent. Nickel-copper ores and lead-silver-zinc ores are mentioned. The use of sulphurous acid in place of sulphuric acid is also specified.

While the underlying chemical ideas described in this patent are excellent, I feel justified in stating that the practical details of flotation in such solutions, the cost of the large amount of chemicals required in many cases, and the difficulties of roasting in other cases, are enough to make the process too costly.

I have recently unearthed a British patent containing a somewhat different idea. It was granted to Sulman & Picard, consulting chemists to Minerals Separation, Ltd., and is numbered 8650 of 1910. While its claims are more broad than here indicated, the particular application is to roast mixed sulphides to oxides; then to treat the roasted ore at about 600° C. with carbon or a reducing gas. Only the easily reducible metals, such as lead and copper, will be reduced to metallic form, while zinc and iron are not affected. Hence, theoretically, at least, it should be possible to obtain a separation. Whether the process works satisfactorily I do not know. It should be a good method for recovering lead and copper left in a zinc concentrate, but it would, of course, be undesirable where the zinc concentrate contains much iron. However, to roast completely, to an oxide, an ore containing zinc sulphide, is a long and costly operation and it has yet to be proved that the subsequent reduction gives a product capable of economical separation by flotation. It is now generally known that metallic copper, in a finely divided condition, can be floated satisfactorily, and it is possible that the same can be done with freshly reduced lead, but there is no certainty that the ore will be in such a physical condition after reduction that these reduced metals can be separated from the other metallic oxides in the ore.

II. **Use of Dissolved Substances.**—The first mention of the use of dissolved substances in obtaining differential flotation was contained in British patent 23,870 of 1910, granted to Henry Lavers, E. H. Nutter, and Minerals Separation. This was probably the first truly differential method on record. Most of the patent is devoted to claims of differential flotation by varying the physical conditions, such as dilution and aeration, but there is also mention of the fact that differential flotation can be obtained by adding soluble substances to the water of the pulp. This patent was also granted in the United States, No. 1,067,485 of 1913. As no specific mention is made of the dissolved substances that effected good differential separation and as the number of dissolved substances that might possibly be used is infinite, it is hard to see why such a patent should have been granted.

Chromates.—The next important process of this kind was that of H. H. Greenway and A. H. P. Lowry, British patent 11,471 of 1913 (also U. S. 1,102,738 of 1914). This consists of treating the ore with a solution of a bi-chromate either before or during flotation. Such minerals as galena and pyrite will be wetted by this solution and minerals like molybdenite, sphalerite, and chalcopyrite can then be floated differentially from their mixtures with either pyrite or galena. The inventors of the process soon learned that much better work could be done by performing the flotation in an alkaline pulp, in the presence of a bi-chromate, and the result of their discovery was embodied in British patent 16,302 of 1913 and U. S. 1,142,820 of 1915. For example, the pulp may advantageously contain an amount of sodium carbonate equivalent to 1% by weight on the ore. This combination of a chromium salt and alkalinity in the pulp is claimed to give particularly good results. Two examples of its success are mentioned in the patent specifications.

The first example is that of an ore containing 9.0% lead, 28.2% zinc, and 14.2% iron, which was finely crushed and then subjected to froth-flotation in apparatus of well-known type by being agitated vigorously with four times its weight of water at 130° F. containing in solution sodium carbonate amounting to 22 lb. per ton and sodium bi-chromate amounting to about 6 lb. per ton of ore. The oil used was a mixture of half a pound of eucalyptus oil with an equal weight of kerosene per ton of ore. The flotation product contained 50.1% Zn, 4.25% Pb, and 8.3% Fe, while the bulk of the iron and lead was left in the residue. Of course, the reaction of sodium carbonate on sodium bi-chromate would be such as to produce sodium chromate, for bi-chromates do not exist in alkaline solution. It is also to be noticed that the percentage of zinc remaining in the lead and iron product is not specified. My own experience in the laboratory with this process is that it is difficult to make as clean a separation as might be desired unless the pulp is heated. In the cold it does not seem to work well unless a long treatment with the chromate solution is given and even then low extractions of zinc are the general rule.

The second example is of slime containing 11.6% lead and 13.4% zinc. This was introduced into an agitator with four tons of water per ton of ore and 24 lb. of sodium carbonate. One pound of eucalyptus oil per ton of ore was used and the flotation was done at 130° F. with the formation of a floating concentrate containing 22.2% Pb and 27.4% Zn. The concentrate was then subjected to differential bi-chromate flotation in pulp containing 24 lb. sodium carbonate and 6 lb. sodium bi-chromate. The oil consisted of 0.75 lb. kerosene and 0.25 lb. eucalyptus oil per ton of ore. The flotation contained 48.6% Zn and 7.5% Pb, while the residue contained 8.9% Zn and 55.9% Pb. This is particularly interesting as it shows that, even after oiling and flotation, the minerals can be so modified by an addition-agent that only one will float. Further, the separation is commonly regarded as good. It is a matter of considerable ease, however, to juggle tests so that they look as well as these in comparison with the test in which only sodium carbonate was used in the pulp. I have noticed that in the flotation of such a mixed ore in an alkaline pulp it is not unusual for the galena to float first, particularly if a small amount of oil is used, and by further addition of oil the zinc can be floated, so that the composite concentrate is much like the first above mentioned. For purposes of obtaining a patent, however, such an experiment is excellent.

Neutral or Alkaline Chlorides or Sulphates.—F. J. Lyster was the next successful inventor to patent a differential-flotation process of this kind, which was assigned to Minerals Separation. His process was first tried by the Zinc Corporation at Broken Hill. It purports to be only an improvement on the fundamental differential patent 23,870 of 1910, mentioned above, and is British patent 11,939 of 1913; also U. S. 1,203,372 of October 31, 1916. This process applies ostensibly to the separation of galena and sphalerite. No heating of the solution is required; it must contain a sulphate, chloride, nitrate, or hydrate of calcium, magnesium, sodium, or potassium, or a mixture of them. It is also possible to use manganese, zinc, or ferrous sulphates, barium chloride, or the carbonate or bi-carbonates of sodium. Under these conditions only the galena floats; the zinc sulphide does

Owing to the fact that the Proprietary company is using a modification of the Potter-Delprat process, no oil need be added when treating a crude ore containing calcite and siderite, as the gas generated by the acid accomplishes the flotation. However, the addition of oil is not objectionable. After treatment in this way, the pulp has to be drained (or de-watered) and re-floated in order to obtain a concentrate carrying the galena. Hence, it may be preferable to make first a mixed concentrate of the two minerals, galena and sphalerite, and then treat the mixed concentrate by this process. In case the mixed concentrate has been obtained by the use of oil, the oil should be removed from the surfaces of the particles by the use of a solution of sodium hydrate, sodium carbonate, or by treatment with ether.

Fine ore often tends to flocculate too fast and the floccules of sphalerite entrain particles of galena. Hence Bradford found it necessary to use an agent that would check or slow down the "flotation tendency." This idea was patented in British 19,844 of 1914. The best substances to use are sulphites and thio-sulphites of the alkaline metals or sulphurous acid, as the latter is generated by the action of the acid in the pulp on these sodium salts. Such a reagent is added to the acidulated brine just before flotation. Too much of these agents spoils the flotation but just the right amount gives a much cleaner concentrate.

British patent 19,373 of 1914 was granted to the Minerals Separation and De Bavay companies for differential flotation applied to zinc and lead sulphide ores, in which the amount of acid largely controls the mineral floated, although a simultaneous control of the amount of oil greatly assists the differentiation. Galena is first floated by the use of a limited amount of oil and too small an amount of acid to effect a separation of both galena and sphalerite from the gangue. On the addition of more acid and more oil the zinc can be separated by another flotation treatment.

When using a circuit-water already containing some oil, the lead can be floated without the addition of oil and the slight acidity of this water does not injure the flotation. The sphalerite

can then be floated by addition of oil and sulphuric acid. If fresh water is used a small amount of oil must be added in order to float the galena.

As an example of the application of this invention the patentees cite the results from treating the slime-dump of a Broken Hill mill. It contained 10% lead and 21% zinc and was used in a circuit-water containing some oil to which was added 22 lb. sulphuric acid per ton of ore. The galena concentrate contained 66% lead and 8.8% zinc from the first flotation-cell, and the average from all the 12 cells of the machine was 50.5% lead and 21.2% zinc. The recovery of the lead amounted to 62.9%.

Commenting on this process: it is probable that any oil in the return-water is only the soluble portion of the oil used. The fact that a great portion of the galena can be floated by the use of this oil is interesting. Sphalerite is known to require more oil than galena and it often requires the presence of acid in the solution. The large amount of zinc in the above concentrate and the low extraction of the lead from such a high-grade heading indicates that the process is not a flattering success.

Acid and Reducing-Agent.—Bradford's work with a "retarder," in the process ascribed to him above, must have brought about the development of this present process. In his first process Bradford floated sphalerite and pyrite in the presence of galena. In this process, covered by British 21,880, of 1914, he floats galena and pyrite in the presence of sphalerite. A slightly acidulated mill-water is used and to this is added a small amount of a reducing agent, like sulphur di-oxide, sodium thio-sulphate, sodium sulphite, or hydrogen sulphide. Bradford has worked almost entirely with sulphur di-oxide or its compounds and states that he does not know much about the action of other reducing agents. He does not confine himself to any particular proportion but states that he has used from 8 ounces to 8 pounds of reducing agent per ton of ore. This renders the zinc sulphide "temporarily immune" to flotation.

Sphalerite can be floated from the residue by de-watering and re-pulping with fresh water, or by the addition of an oxidizing

agent, or by warming and aerating until the sulphur di-oxide and sulphites are oxidized. An excess of reducing agents delays the flotation of both galena and sphalerite, because the excess of reagent has to be oxidized by the aeration given the pulp in the machines until the galena can float, and later, when further oxidized, the sphalerite can float. Only enough reducer should be added to render the blende temporarily immune. Heat is not required but assists greatly, as the oxidation of the reducing agent takes place much faster and thereby the sphalerite is all the sooner ready to float after the galena and pyrite have been floated. The apparatus recommended by Bradford is a string of centrifugal pumps and separating-boxes in order that aeration can be controlled. Occasionally, the results are greatly enhanced by giving the pulp a previous digestion with acid and the reducer before flotation.

This patent quotes a number of excellent examples of tests made according to the method described. In one test a 500-gm. lot of ore was treated in three litres of water containing one gram of sodium thio-sulphate and enough sulphuric acid to make the water react acid, and enough of the regular frothing-agent. This ore was a Broken Hill weathered dump-slime, which was partly oxidized. The results were as follows:

	Gm.	Zn, %	Pb, %	Ag, oz.
Heading	500.0	18.2	15.2	18.3
Lead concentrate	79.5	9.6	60.0	69.0
Zinc concentrate	166.5	46.4	6.3	15.7

The zinc concentrate was obtained after the lead concentrate had been taken off by the addition of 0.1 gm. of potassium permanganate to oxidize the sodium thio-sulphate.

In another test with a pyritic blende ore the use of sulphurous acid prevented the flotation of the blende while the pyrite was removed. By thickening the pulp and discarding the sulphurous acid solution, it was possible to obtain a residue from which the zinc could be floated after re-pulping with fresh water. The table of results is as follows:

	Gm.	Zn, %
Heading	500	28.3
Pyritic concentrate	148	13.4
Zinc concentrate	220	51.6
Tailing	120	3.7

Hydrochloric Acid and Zinc Chloride are supposed to sink galena and sphalerite in the presence of other sulphides, supposedly pyrite and chalcopyrite, as well as the sulphides of silver. This combination is mentioned in a German patent, 282,131 of 1915, granted to E. Languth of Neerpelt, Lembourg, Belgium. Nothing seems to be known of it beyond the statement that an acidified zinc-chloride solution is used.

Alkaline Solutions.—British patent 9049 of 1914 was granted to the Amalgamated Zinc (De Bavay's), Ltd. for the use of alkaline and other solutions. Galena is wetted differentially in the presence of sphalerite. The patent recommends that a combined zinc and lead concentrate be obtained by ordinary flotation and that the combined concentrate of galena and sphalerite be re-treated in dilute sodium-carbonate solution. The galena, wetted by the solution, sinks while a froth rich in sphalerite is obtained. It is also recommended that if a mixed concentrate has been obtained by the use of an organic frothing-agent it should be first treated with a solution of hydrogen sulphide, sodium sulphide, sodium sulph-hydrate, or other such agent added to the sodium-carbonate solutions.

I do not pretend to understand this process, as all my experience tends to prove the contrary: that galena is more easily floated differentially in the presence of sphalerite in a slightly alkaline solution. A reference to the paper [3] of Palmer, Ralston, and Allen on the subject of "Some Miscellaneous Wood-Oils for Flotation" will show that in neutral and in alkaline solutions most of the oils tested gave differential flotation of the galena.

In U. S. 1,203,373 of October 31, 1916, Lyster claims the use of solutions containing alkalies like sodium carbonate (500 gr. per gal. water) or sodium bi-carbonate (600 gr. per gal.). This

[3] Bull. 116, A. I. M. E., Aug., 1916, pp. 1387–1396.

patent accompanies others claiming the use of alkaline solutions of chlorides or sulphates of the alkalies and alkaline earths.

Alkaline Sulphides.—British patent 8746 of 1915, granted to Minerals Separation, covers the use of sodium or similar sulphides in the differential flotation of galena in the presence of sphalerite. It also mentions that occasionally the addition of sodium carbonate or of a bi-chromate is helpful, and that a frothing-agent may or may not be used and that the solutions may be heated if so desired. Pyrite is also said to be floated differentially in the same manner, and the sub-aeration machine is recommended. Beyond the mention of bare facts and claims this patent does not tell much; no statement of general principles is given and it is only claimed that the " chemicals are varied to suit the ore used," with no suggestion as to how this point can be determined except by " experiment." It is not even claimed that sodium sulphide has any advantage over other alkaline reagents and nothing is said about the fact that sodium sulphide is a reducing-agent. We have seen the use of a reducing-agent, such as the sulphur di-oxide, or sodium sulphite under acid conditions, patented by Bradford. The result is the same as in Bradford's patent, the differential flotation of galena and of pyrite in the presence of sphalerite. These patentees say:

" The process is usually carried out in a circuit containing in solution about from 0.1% to 1% of a sulphide of an alkali-metal or earth, such as sodium sulphide. The solution is preferably heated to 130 to 140° F. and is used with or without a frothing-agent. In certain cases, the addition of a small amount of about 0.1% to 0.5% of an alkaline substance, such as sodium carbonate, may be made, while in other cases the addition of a small quantity of a bi-chromate of an alkaline metal, such as potassium or sodium bi-chromate, will be found advantageous."

In giving the details of a number of illustrative tests, mention is made of the use of a " sub-aeration vessel constructed of wood or iron " but no reason is given for this stipulation. Evidently cast-bronze or aluminum test-machines are taboo.

Manganese Compounds.—T. MacKellar Owen has been granted U. S. patent 1,157,176 of 1915 for the use of alkaline per-

manganates in solution for accomplishing differential flotation of various sulphides. " In the froth-flotation treatment of mixed sulphide ores containing, for instance, lead, copper, zinc, and iron sulphides, or any two or three of these sulphides, the introduction of a small quantity of an alkaline permanganate into contact with the slime, makes the flotation operation selective in the case of a large range of representative slimes. In the case of lead-zinc slime the galena and the blende are raised in successive order; the galena is floated first, the bulk of the silver if present, accompanying the galena, and the blende is subsequently floated from the residue after acid has been added to the pulp. If copper is present it usually comes up with the lead.

" The proportion of alkaline permanganate required is less than the quantity that would be necessary to change permanently the reducing character of the mass of the pulp. Relatively minute quantities of free alkaline permanganate will substantially affect the behavior of certain metallic sulphides in the flotation liquor. . . The pre-treatment of the water with permanganate to neutralize its reducing quality does not produce the same effect as having the permanganate present in the pulp acting on the slimes during its dissociation." It is most advantageous to add the permanganate after the slime has been mixed with the flotation liquor as, otherwise, it seems to be wasted in oxidizing impurities of the water and more quickly results in " sickening " of the circuit-liquor. " Manganese di-oxide may be used to procure effects of the same order as alkaline permanganate." When the slime is of a very reducing character and quickly decomposes the permanganate, it is advantageous to conduct the process at a temperature of approximately 120° F.

" I quote the case of a weathered slime obtained from the treatment of an ore obtained at Broken Hill, N. S. W., said slime containing approximately by assay 16% Pb, 13.5% Zn, and 17 oz. Ag per ton. In this treatment, using 2.5 lb. of potassium permanganate, and 3 oz. eucalyptus oil per ton of slime, a lead concentrate was obtained containing 60.5% Pb, 54 oz. Ag, and 11.8% Zn, and after adding 15 lb. of sulphuric acid per ton of original slime, a zinc concentrate containing 6.2% Pb, 11.2 oz. Ag, and

43.4% Zn, leaving a residue containing 2.0% Pb, 3 oz. Ag, and 1.6% Zn.

Owen describes the operating details of his process most frankly. The patent specification is pleasant to read and I regret that it is too long to be reproduced in full. If acid is added in any quantity to the pulp before the lead is removed it is impossible to get differential flotation, the lead and zinc sulphides tending to float together. In practice Owen recommends the use of a separate circuit-liquor containing the manganese compounds for flotation of the lead, followed by de-watering and re-pulping with new water for the flotation of the zinc. This makes two water-storage tanks necessary. Since the manganese liquor tends to " sicken " with repeated use, an effort is made to exclude contaminations and to introduce fresh water at this point rather than some other in the system. Certain cases, which cannot be definitely defined, are found in which the process is commercially ineffective, notably a few cases of mixed iron and copper sulphides. Only a laboratory test will tell. For some slimes a preliminary weathering of a few hours will greatly improve the results, and hence it is advisable to make experiments in the laboratory and take account of this possibility.

Copper or Mercury or their Compounds.—British patent 4974 of 1915, to Minerals Separation, covers the use of metallic copper or mercury or a compound or alloy of either of the metals, in differential separation of a froth rich in zinc from a mixture of the sulphides of lead and zinc. Preferably the operation shall be carried on in a brass or a bronze vessel. The invention is applicable to other differential processes patented by Minerals Separation or its engineers, one example being the use of chromium compounds mentioned by Lavers. The copper metal can be placed in the flotation machine in any convenient form such as a sheet-copper lining, or it may be introduced with the pulp in finely divided form.

Copper Sulphate.—The above mention of the use of metallic copper and copper compounds for differential flotation evidently does not extend to the use of soluble compounds of copper. A

minute amount of copper sulphate in solution in the mill-water seems to improve the flotation of sphalerite. It has been used for this purpose in the mill of the Hercules Mining Co., at Wallace, Idaho, with only indifferent success, as the object is to drop some of the pyrite, which tends to enter the zinc-lead concentrate. While improved results are obtained, there is still too much iron in the zinc concentrate.

Chlorine and Chloride of Lime.—The use of chlorine in an active form, such as is obtained by the use of chloride of lime, seems to be successful in the treatment of products containing sphalerite. In one Canadian plant iron sulphides are wetted by such a solution. Its use in the United States has been kept secret. However, the employment of chloride of lime for flotation of galena in the presence of sphalerite has been patented in England (10,478 of 1915, granted to Minerals Separation). Considerable success has been claimed for this reagent and it is hoped that information will be forthcoming in the near future. It may be that chloride of lime has much the same effect as that observed in the use of ordinary slaked lime at the Midvale plant, Utah, where some lessees of an old dump claim to have prevented the flotation of iron by the use of 8 lb. of lime per ton of ore, both sphalerite and galena being floated.

III. **By Physical Control.**—One of the most important and fundamental processes for obtaining differential flotation is disclosed in the patent of E. H. Nutter, Henry Lavers, and Minerals Separation (U. S. patent 1,967,485 of 1913, and British 23,870 of 1910). This patent probably grew out of observations on the changes of froth produced by varying physical conditions during flotation. The factors mentioned are "agitation, aeration, chemical constitution of the solution employed, the degree of dilution of the pulp, the temperature, and the amount and character of the frothing-agents." The purpose seems to be to claim the idea of differential flotation in general and the Minerals Separation people evidently regard it as their basic patent in this line. In fact, most of their subsequent patents in differential flotation refer to this one, stating that they are improvements and that they merely supplement it.

The best idea contained in the patent is that occasionally, by controlling physical conditions in just the proper way, a froth containing the minerals in certain ratios of size will be obtained, such as a froth containing most of the copper sulphides of an ore, some fine sphalerite, and some still more finely divided gangue. After breaking down such a froth the mixed froth can be tabled to separate the various minerals. After obtaining several different froths by close attention to any of the above conditions it may be possible to separate a complex ore by tabling.

One of the important physical conditions affecting differential flotation seems to be the variety and amount of the oil of frothing-agent. For example, the process in the patent of T. M. Owen (British 16,141 of 1913) taken out by Minerals Separation, is designed to treat a mixed zinc-lead sulphide ore. By the use of a limited amount of frothing-agent in a neutral or an alkaline pulp, the galena can be floated in the presence of sphalerite, and then by the addition of more oil, or by more oil and some acid, the sphalerite can be floated. This method is in general use throughout the Northwest, both in the United States and in Canada. Most of the companies are secretive, however, and do not wish to allow publication of the details of their practice. Suffice it to say that they are making commercial grades of concentrate but that the separation is never quite clean, and too much zinc is left in the lead concentrate and too much lead in the zinc concentrate. I am informed that this process is at work in the Hewitt mill of the Silverton Mining Co., at Silverton, B. C. The gangue contains much siderite and the sulphides are galena, sphalerite, and silver sulphides. The ore is crushed, and the coarse galena tabled. The slimed galena is floated differentially in a 2-cell M. S. machine, giving a concentrate carrying 52% Pb and 6% Zn, while the zinc is removed in a 10-cell machine giving a product carrying 45% Zn and 2% Pb. The silver goes with the lead, and the extractions are said to be 85% of the lead, 90% of the silver, and 86% of the zinc. This is unusually good work.

Owen describes the treatment of slimes at the Broken Hill South mine. Ordinary temperatures suffice and no acid. The

lead is removed in the first three cells of an 11-cell machine by the use of one ounce of eucalyptus oil per ton of ore. This gives a recovery of 85% of the lead in a product containing 60 to 79% lead. By the addition of more oil and some sulphuric acid 70% of the zinc in the ore can be recovered in a concentrate carrying 46% zinc.

Following Owen's patent came one taken out by the Minerals Separation and De Bavay companies, British 19,374 of 1914. It purports to be an improvement over Lyster's and over the basic differential patent 23,870 of 1910. It is designed for differential flotation of galena-sphalerite mixtures. The claim is that too small amounts of oil to float both sulphides will float only the galena and will give a clean separation in either neutral or alkaline pulp; in other words, flotation conditions are so poor that only the most easily floated mineral, the galena, is separated. The zinc in the residue can be caused to float by the use of more oil, with or without the addition of acid. Aeration and emulsification are claimed to have no effect on the zinc as long as the amount of frothing-agent is below the maximum required for the lead alone. This maximum is dependent on the condition of the circuit-water and the amount of dissolved salts therein. While aeration is said to have little effect on the zinc, it is to be noticed that usually the sub-aeration machine is recommended for the flotation of the galena in most of these patents and sub-aeration machines or pneumatic machines seem to be best adapted to the flotation of this mineral.

This method of flotation is in use by the Sulphide Corporation at its Central mine, treating the slime-tailing from the table concentration in a Hebbard machine. The feed averages 4.2% lead and 18% zinc, while the lead concentrate assays about 50% lead. The residue from the first three boxes assays 0.53% Pb and 18.5% Zn. The zinc concentrate assays 6% Pb and 47.5% Zn and the tailing 1% Pb and 2% Zn. The recovery of lead is rather low.

It also happens that during grinding one mineral will be slimed while another will not be so thoroughly ground. Galena and chalcopyrite are two rather friable minerals and as galena

usually accompanies sphalerite, and chalcopyrite usually accompanies pyrite, it is these two separations that are of interest. As a rule there is little difficulty in getting a marked separation of galena from sphalerite, owing to this fact alone, and likewise a separation of chalcopyrite from pyrite. For the flotation of chalcopyrite the plants of the Calaveras Copper Co., and of the Mountain Copper Co., in California, as well as that of the National Copper Co., in Idaho, are examples.

The Minerals Separation company has taken out a British patent, No. 5650 of 1915, that claims the addition of finely divided carbon to a pulp in order to gather the galena in preference to the sphalerite. Any finely divided form of carbon, charcoal, or coke is said to be satisfactory. Preferably an alkaline pulp should be used. The finely divided carbon probably depletes the pulp of oil so that a minimum amount of oil in a slightly alkaline pulp with excessive aeration can be obtained for the differential flotation of the galena. This is only a guess on my part but I believe that the absorbent power of the finely divided carbon for oil is the physical result involved. If the oil in the pulp is largely absorbed by the carbon, only the galena can get enough oil to float. The carbon goes into the froth and the galena accompanies it. Recent work at the Magma Copper Co., in Arizona, by the General Engineering Co., of Salt Lake City, has developed a fairly successful differential flotation of sphalerite from pyrite. A small amount of oil, together with an alkaline pulp and excessive aeration in Callow cells, aids the flotation of the sphalerite. This is improved by the addition of a small amount of copper sulphate. As little as a tenth of a pound of copper sulphate per ton of ore has a noticeable effect. A 45% zinc concentrate and a 4% tailing is made from a 15% zinc heading.

What Kind of differential flotation is most desirable? The usual answer of the technical man is, " That depends on circumstances." The circumstances under which a slime needing differential flotation is generally produced are those obtaining in a gravity-concentrating mill. It is awkward to de-water the slime

and give it the fractional roasting demanded by some of the patentees. There is no point in de-watering the pulp, roasting it, and then putting it back into the water for further flotation if there is a possible method of getting the same results without so much trouble. The simple addition of a small amount of some chemical to the pulp or the careful control of the amount of oil used offers a much less expensive process. The de-watering and filtration of a slime often costs 20 cents per ton and a roast might cost all the way from 25c. to 75c., with attendant dust-losses. Against these costs are to be set the amount of chemicals consumed or the extra power expended when minute amounts of oil are being used in order to obtain flotation of only one mineral. However, where the ore can be obtained in a dry state with no special effort it may pay to use the roasting method of modifying the easily burned minerals before flotation. Dust from an electro-static or an electro-magnetic plant, or from other dry-concentration processes, is already in a condition for such treatment. Moreover, roasting is the only sure way of rendering iron pyrite non-flotative. In the case of zinc ores this may be well worth while, as the smelters do not like to take much iron in the concentrate. The wonderful resistance of zinc sulphide to roasting grieves the zinc-smelter men but the above method takes advantage of this resistance. A mixture of zinc and iron sulphides can be roasted at about 600° C. for as much as two hours, causing but little oxidation of the zinc sulphide and almost complete oxidation of the pyrite. The ore does not even have to be finely ground for this work and can be more easily pulverized for flotation after the roast than before. I have witnessed a separation of one particularly difficult ore containing marmatite and pyrite. The purest piece of marmatite contained 12% iron and much of it contained more. Of course, the iron in the marmatite could not be separated, but by roasting till the iron from the pyrite was almost completely converted into red oxide the marmatite could still be floated. The concentrate assayed 49% zinc and 21% iron, and looked almost blood-red. This was made from ore containing 13% zinc and 19% iron, which could not be

separated by any other means, and while the flotation product was still far too high in iron to be acceptable at the zinc smelter, the point to be noted is the wonderful resistance of zinc sulphide to alteration.

The question arises how best to apply differential flotation. Shall a mixed flotation concentrate of the several sulphides be made first and then only this small bulk of higher-grade product be subjected to differential flotation or would it be better to apply the differential-flotation methods to the crude ore?

It is probable that a flow-sheet in which only a concentrated product is treated by the specialized methods described here would allow of more careful work, closer supervision, and the use of more expensive chemicals than could be applied to the bulk of the crude ore. This principle should apply to all the methods in which the previous concentration by flotation does not spoil the mineral particles for one of the differential schemes. Such a process as the one in which only a minute amount of oil is added to float the galena of the ore, followed by the addition of more oil to float the remaining sulphides, would be impossible if applied to a mixed flotation concentrate because this concentrate already contains too much oil for the application of the process. It is doubtful if the oil in a flotation concentrate can be removed by any of the proposed methods sufficiently to warrant the application of this process. The use of powdered carbon might be of value in this connection for absorbing some of the excess oil.

The Elements of Simplicity should be sought in differential work. Any of the methods of differential flotation that involve de-watering and re-pulping should be avoided, if possible, on account of the space and cost of thickeners and the large amount of water used. Some method requiring a simple addition of oil or acid in order to float one mineral after a first has been floated will commend itself. Avoid also the use of a solution that can be so changed by continual use that it sickens and has to be discarded. It will be recalled that Owen's process, using alkaline permanganates, is one of this type. A sodium-sulphide solution

is likely to oxidize to thio-sulphates or sulphites, which, if present in sufficient amount, entirely inhibit flotation. Avoid the use of a solution of a valuable chemical that must be washed out of the tailing and recovered. The solution containing zinc chloride or the one containing chromates is an example. Avoid the use of addition-agents that, in order to be effective, require some length of time in contact with the ore. Heating of solutions, unless by waste heat from some other operation, is also to be avoided. Finally, do not use a method of differential flotation that is sensitive and requires constant attention.

When differential flotation depends on the addition of some chemical, the supply of that chemical and the facilities of transportation to the mill have to be considered. Sulphuric acid is not well adapted to carriage by wagon in mountainous districts. Many of the reagents are expensive when bought on the market but they can be cheaply made at the mine. For example, I have heard Owen's alkaline permanganate solution decried on the ground that "potassium permanganate is entirely too expensive a chemical for commercial work." No one said that the potassium salt had to be used and Owen's claim was that most manganese compounds were suitable. Manganese ores are often available locally and the fusion of some of this ore with crude soda will give an inexpensive sodium manganate. Lime is a cheap chemical, easily available in most mining districts, and hydrogen sulphide can be made from pyrite, other sulphides, or even elemental sulphur. Likewise, sodium chloride, common salt, is well distributed over the face of the earth and is not far distant from most mines. The chromates are the only reagents recommended that might be difficult to obtain.

There is only one case where a substitute for differential flotation seems to be having any success, namely in the separation of the zinc and lead sulphides. A pulp that will not separate well by ordinary tabling methods may yield to a method wherein the mixed sulphides of zinc and lead are floated together, the froth broken down, and the pulp passed over a Wilfley or other table. Under these conditions a streak of lead, well-de-

fined and sharply differentiated from the zinc, can be obtained, whereas the gangue-slime may prevent any gravity-separation before flotation. Some people have gone so far as to believe that the oiling of the surfaces of the particles has improved the tabling qualities. It is probable that the only effect is the breaking up of the lumps of mixed mineral during the agitation for flotation.

The most pressing problem in differential flotation is the removal of pyrite from a sphalerite concentrate made by flotation. Mixtures of zinc and lead sulphide are not so hard to get apart. If a previous fractional roast is given before milling there is usually no difficulty from the flotation of iron, and the zinc will still float; but if flotation is used in a wet mill to treat only the slime, and a zinc concentrate badly contaminated with iron is formed, the separation of the iron will be difficult indeed. The most successful addition-agents for dropping the iron during flotation seem to be oxidizers like the chromates and chloride of lime. Chlorine improves the flotation of sphalerite and lime tends to drop iron. Copper sulphate likewise seems to improve the flotation of sphalerite but at the same time tends to improve that of pyrite. Fortunate is he who has the ore in which the pyrite does not tend to slime to the same extent as does the sphalerite, or where the pyrite is already weathered to a condition in which it is difficult to float. At Crown King, Arizona, a mixed flotation concentrate of zinc and iron sulphides is passed over a Wilfley table with the result that the oil is washed off the pieces of pyrite. On subjecting this pulp to a second treatment only the sphalerite is floated.

Summary.—The factors used in differential flotation either to assist the flotation of one particular mineral or to retard its flotation are tabulated for four of the principal sulphide minerals. These are the factors on which the various processes are based. The abbreviations "As." and "Ret." mean "assisted" and "retarded" respectively.

Factor.	Sphalerite.		Galena.		Pyrite.		Chalcopyrite.	
	As.	Ret.	As.	Ret.	As.	Ret.	As.	Ret.
Acids	*				*		*	
Weakly alkaline solutions		*						
Lime						*		
Sodium sulphide					*			
Chloride of lime	*					*		
Chlbrine	*					*		
Limitation of oil		*				*		
Chromates				*		*		
Permanganates, etc		*						
Neut. or alk. chlorides		*						
Weakly acid chlorides				*				
Sulphur di-oxide, etc		*						
Roasting or weathering				*		*		
Dry grinding						*		
Heated solutions	*							
Fine grinding			*				*	
Zinc chloride and HCl		*		*				
Metallic Cu and Hg	*							
Copper sulphate	*							
Reducing solutions		*	*		*			
Oxidizing solutions	*			*		*		
Aeration			*					
Washing in fresh water						*		

FLOTATION AT THE CALAVERAS COPPER—A SIMPLE FLOW-SHEET [1]

By Hallet R. Robbins

Introduction.—The Union mine is situated in the foot-hills of the Sierra Nevada in the extreme southern part of Calaveras county, California. The town of Copperopolis, with a present population of about 600, has grown up around the mine, and is reached by road from Angels Camp, 12 miles; Stockton, 42 miles; or Milton, 17 miles. The mail is carried by automobile-stage daily except Sunday over the last route, and there is also regular auto-stage service from Stockton. Surveys have just been completed, and construction is about to be started, on an extension of the Southern Pacific railroad from Milton to Copperopolis.

This is one of the oldest and most interesting metal mines in California. It was discovered by placer miners in 1859, and soon afterward one portion of the lode was acquired by Frederick Ames of Boston, and another, called the Keystone mine, by Oliver Ames. The Union Copper Mining Co., organized by the former, subsequently absorbed the Keystone property, as well as several smaller holdings on other portions of the lode. Operations were conducted by the Union Copper Mining Co. on a large scale. During each of the years 1865 and 1866 about 23,000 tons of ore, averaging over 20% copper, was shipped to Swansea, by wagon to Stockton, by river-boat to San Francisco bay, and finally by sailing-vessel around the Horn. A stone blast-furnace was erected and operated on second-class ore averaging 10% copper, using charcoal as fuel. The matte was shipped to Swansea. No statistics are available as to the tonnage treated in this smelter.

[1] From the *Mining and Scientific Press* of November 25, 1916.

The fall in the price of copper following the Civil War, as well as the high cost of transportation, caused the mine to be closed-down in 1867, in which condition it remained until 1887, when there was a renewal of activity at the property, culminating in the erection, in 1891, of another blast-furnace smelting-plant, which ran about two years, and produced 150,000 tons of slag.

Operations were again suspended in 1893, the mine remaining idle until 1905, when a gravity-concentration mill and a third smelter were built. The mill did not run longer than a week or two at this period, but the smelter ran about two years on first-class ore. Heap-roasting was practised, the calcine being smelted in a 50 in. by 7 ft. reverberatory furnace, producing a 50% matte, which was shipped to a refinery at Chicago.

The panic of 1907 caused another suspension of operations, lasting until 1909, when the Calaveras Copper Co. was organized and took over the property on a bond. The smelter was rebuilt, and two 20-ft. six-hearth McDougall roasters were erected. The plant proved unworkable after two weeks' trial, and then a 40 by 120-in. blast-furnace was built, but it ran for two weeks only. Converting equipment was purchased and delivered, but never installed. The mill was operated intermittently at this time, but did not make over a 50% saving.

In September, 1914, a capable and efficient manager in the person of S. M. Levy, of Salt Lake City, was appointed, under whose guidance, with the assistance of E. C. Trask, mill foreman, D. C. Williams, mine foreman, and Frank W. Royer, consulting engineer, the property has been firmly placed on a paying basis and has become one of great promise.

The Orebody is a replacement in amphibolite schist; it is from 100 to 200 ft. wide, with slate hanging wall and serpentine foot-wall. The valuable minerals are chalcopyrite, containing no gold or silver, and, near the surface, red and black oxides of copper. The lode is free from serious faulting, it strikes north-west, dips 61° north-east, has been fully developed for a length of 1500 ft. and to a depth of 800 ft., and is known to persist over a length of three-quarters of a mile. There is every indication

of persistence in depth, as well as to a greater distance along the strike.

The most striking peculiarity of the ore is the association of a large amount of barren pyrite with the chalcopyrite. This is the explanation for the many failures to exploit the mine, for when gravity concentration was attempted, the pyrite was saved, while the chalcopyrite was largely slimed and lost.

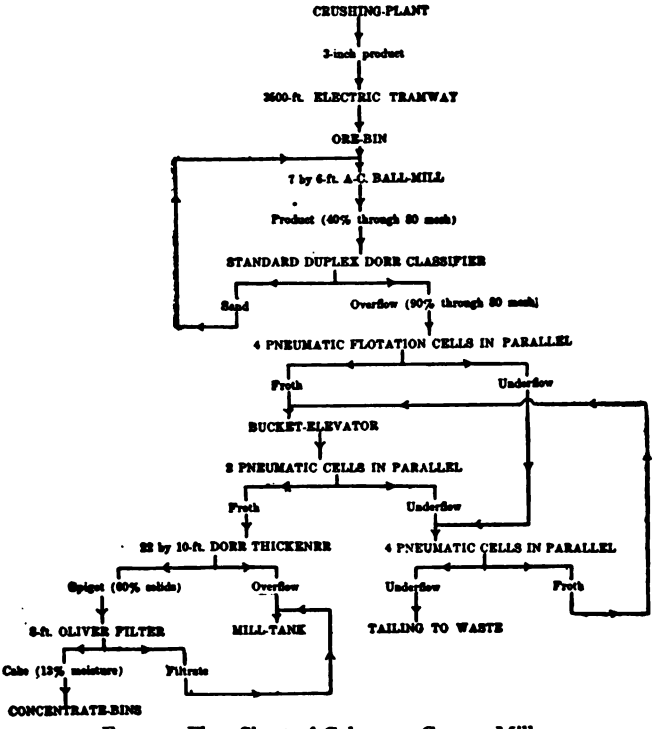


FIG. 1.—Flow-Sheet of Calaveras Copper Mill.

The Mine is opened by two working-shafts, the Union and the Discovery. The former is 800 ft. deep, vertical to the 5th level, and on an incline of 63°, following the lode, from there to the bottom. It was sunk in the 'sixties, and is equipped with a wooden head-frame, 35 ft. high, and with a double-drum hoist with both steam and electric drive.

The Discovery shaft is in the lode, on the hanging-wall side,

and is now 400 ft. deep, measured along the 61° incline, but is being connected with the 9th level by raising. It is equipped with an excellent steel head-frame, 80 ft. high, erected in 1902 at a cost of $10,000, and good for four compartments, though the shaft now has but three; and with a steam-driven double-drum hoist, good for 1500 ft., and with a 1500-cu. ft. compressor driven by a 275-hp. motor.

The stopes are 15 to 30 ft. wide; the shrinkage method is followed, at a cost of 50 cents per ton. The total cost of mining, including timbering, hoisting, development, etc., with the present daily production of 200 tons, is $1.50 per ton. It is expected that this will be reduced to $1.25, as soon as the production is increased to 500 tons per day, which is the maximum output expected at present.

The force employed includes 2 shift-bosses at $4; 10 machine-miners at $3.50; 4 timber-men at $3.50; 4 timber-men's helpers at $3.25; and 22 shovelers at $2.75.

Ingersoll-Rand stopers are used for stoping and raising, jackhammers for sinking and block-holing, and Denver Dreadnought water-drills in the drifts.

The mine is considerably wetter in winter than in summer. In the wet season, one 4½ by 7-in. triplex pump is operated 24 hours daily, raising all the water made by the mine, from the 8th level to the surface. In the summer it is run only six to seven hours per day.

Flotation.—Experiments began in December, 1914; in February, 1915, the so-called " little mill " was started on accumulated tailing from the old gravity-mill, containing about 1.5% copper. The equipment consisted of one Huntington mill, grinding through 50-mesh; a mechanical agitator; a pneumatic flotation-cell, making a final tailing and a rough concentrate; and a Wilfley table, making a final concentrate and a middling that was returned to the Huntington. In May, 1915, the treatment of accumulated tailing was discontinued, the " little mill " after that date handling 25 tons per day of undersize from the 1-in. trommel at the picking-plant. The oversize, after the first-class ore had been picked out, was treated in the " big mill," which

was the old gravity-mill with some experimental flotation equipment, handling 60 tons per day, with much the same flow-sheet as in the "little mill," so that further description is not necessary.

The results of this operation indicated that from a mill-feed assaying 3% copper, 28% iron, 20% sulphur, 20% silica, and 10% alumina, there would be obtained a concentrate assaying about 19% copper, 30% iron, 35% sulphur, and 6% insoluble, with a ratio of concentration of 7 : 1, and a recovery of 90%.

These operations also indicated that the most efficient oil was

FIG. 2.—Air-Pans of Flotation-Cell.

Yaryan steam pine-oil, and that mechanical agitation of the pulp before flotation was necessary for the best results.

The old gravity-mill, which was housed in a well-built and substantial steel-frame building, was then further re-modeled, and in March, 1916, operations began according to the flow-sheet shown in Fig. 1. These operations have been remarkably successful.

Present Practice.—The extreme simplicity of the plant and the entire absence of any gravity concentration are very striking. The ball-mill has a normal capacity of about 8 to 9 tons per hour. The reduction in one mill from 3-in. size to a product 90% of which passes 80-mesh would not be economical in a large plant, but in a

small one the simplicity of the arrangement is commendable. The mill is driven through a counter-shaft, by a 150-hp. motor, at a speed of 23 r.p.m. The normal power consumption when running is 120 hp. Forged steel balls, 5 in. diam., are used, the consumption being 0.5 lb. per ton of ore ground. Of the total product 40% is finished through 80-mesh, the remainder being returned by the classifier. The mill has given reasonable satisfaction, the most serious difficulties being blinding of the difficultly accessible grating, leakage around lining-bolt holes and dropping-out of lining-bolts, and a peculiar ailment, not as yet fully diagnosed, but probably due in part to the wear of the lining, that at times has caused the capacity of the mill to drop practically to zero. When the mill was opened on such occasions the ore and balls were found in quite separate masses. Increasing the speed from 21 r.p.m., as recommended by the makers, to 23 r.p.m. proved beneficial in minimizing this trouble.

Difficulty has also been encountered in the buckling of the lining-segments, which are the full length of the mill, thicker on one edge than on the other, in order to form steps to lift the balls and cause them to cascade properly through the charge of ore. They are held by three bolts in a line along the centre of each segment. The edges of the segments draw away from the shell, and the lining requires to be discarded and renewed when only about half the metal has been worn away. Similar troubles have been reported at other plants, and it is my belief that they may be overcome by the use of lining in full annular sections, wedged in place, with no bolt-holes whatever through the shell. Such sections may be secured from the Lehigh Car Wheel & Axle Co., and are being tried by the Utah Copper Company.

The oil adopted as standard in the present operation, after exhaustive experiments, is the No. 400 crude wood-creosote produced by the Pensacola Tar & Turpentine Co. The No. 350 crude pine-oil produced by the same company was recently tried on a 24-hour run, with a marked increase in the value of the tailing, and a decrease in the grade of the concentrate. A mixture of equal parts of No. 17 hardwood-creosote, and No. 20 coal-tar creosote, furnished by the General Naval Stores Co.,

has given better results than any oil except that regularly used.

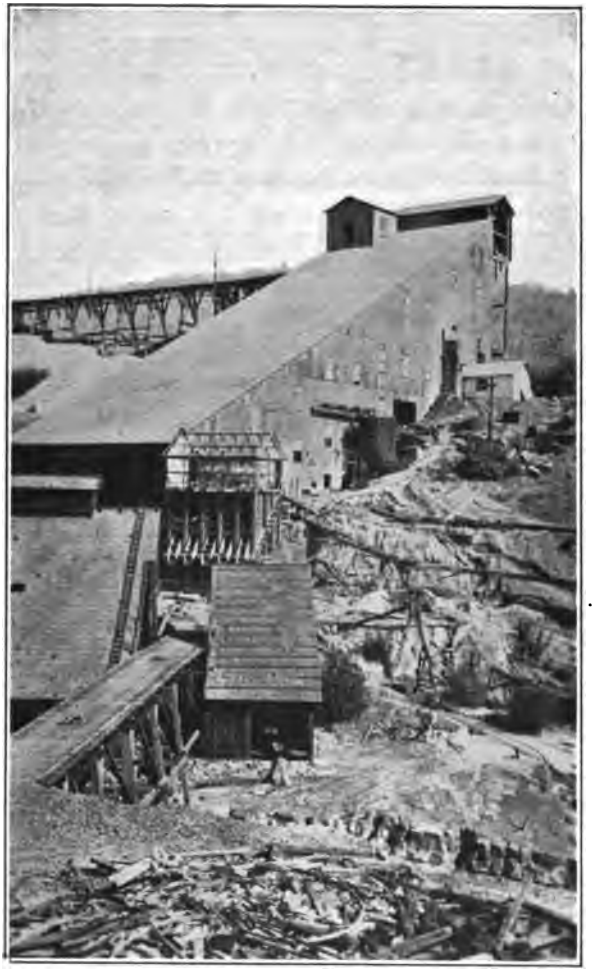


FIG. 3.—The Calaveras Copper Mill.

The oil is all fed into the ball-mill feed-box from a 15-gal. zerolene can, fitted with a special bronze stop-cock. The consumption averages 0.3 lb. per ton of ore. It is so well mixed

and agitated in the ball-mill that neither mechanical nor pneumatic agitation before flotation is found of any benefit whatever.

The return of the filtrate from the concentrate-filter and of the overflow from the concentrate-thickener has been found not only to decrease the amount of oil required, but also to effect a closer saving than is possible otherwise, no matter how much oil be used.

The flotation-cells are made locally from Oregon fir, protected with P. & B. paint, at a cost of about $100 each, complete. They are of the type for which J. M. Callow has had process and apparatus patent-applications pending in the United States for some time. The porous bottom differs from that used by Mr. Callow in the cells he has built. It is composed of eight separate shallow cast-iron pans, placed side by side along the sloping bottom of the cell, each covered with a multiple-ply canvas, fastened around the edges only. Screens or grids, similar to those used by Mr. Callow, were tried but proved both unnecessary and objectionable.

The outside length of each pan is a trifle less than the inside width of the cell. Two $\frac{3}{4}$-in. pipes are screwed into the bottom of each pan, and pass through holes bored in the wooden floor of the cell. One is connected by means of an easily-removable length of hose, to the air-main manifold, and the other is fitted with a plug-cock, normally closed, but opened periodically to blow out accumulations of water in the pan.

When it is desired to remove a pan, the air-hose is disconnected, and the plug-cock unscrewed, when the pan may easily be lifted from the cell. When the cell is in operation, the holes through which the air and water blow-off pipes pass, are caulked with oakum. This form of air-pan was an original development at Copperopolis, but resembles that developed previously at McGill, Nevada, and used in the pneumatic flotation-cells of the Nevada Consolidated Copper Co. A photograph of two of the Copperopolis air-pans, one right-side up and the other bottom up, is shown in Fig. 2.

A detail drawing of the flotation-cell as a whole, from which one may be built by any competent carpenter, is shown in Fig. 4.

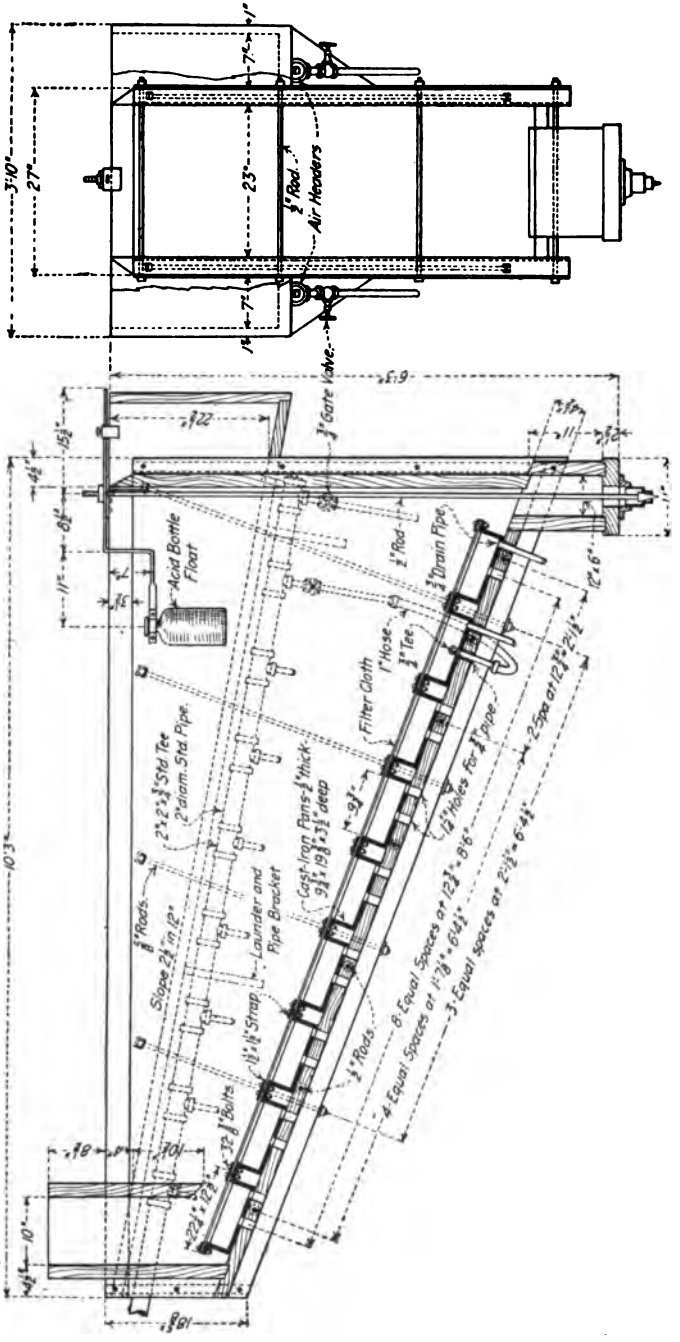


FIG. 4.—Flotation-Cell in Calaveras Copper Mill, California.

Air is furnished at 5½ lb. pressure by a Connersville blower. The consumption is about 80 cu. ft. free air per minute per cell. Each cell is emptied once per day and the surface of the canvas is washed off with a hose. The canvas lasts several weeks, and when a renewal is necessary, it is effected quickly by removing the pan in the manner described, and replacing it with one already freshly clothed.

The air-supply is not filtered, but I believe it is good practice to do so in all cases where porous media are used in flotation-cells. During the past two years I have visited nearly every flotation plant of consequence in the West, and have seen no pneumatic cell frothing so smoothly and evenly as those at Copperopolis.

Some interesting experiments have been made in heating the thickened concentrate in the filter. At some plants where this has been tried, it was found possible to make a cake of double or treble the usual thickness, with no increase in the moisture content. This is probably due to the heat decreasing the viscosity of the oil in the pores of the filter-canvas.

The results of the operation of the plant may be appreciated from the following assays of composite samples for the month of June, 1916:

	Copper, %	Iron, %	Insoluble, %
Heading	2.15	20.4	37.0
Concentrate	14.40	29.5	14.9
Tailing	0.09	18.0	43.4
Rough concentrate	8.0	....	....
Cleaner tailing	2.0	....	....

Ratio of concentration, 7 : 1.
Saving of copper, 96.4%.
Saving of iron, 30.2%.

It will be interesting to compare these results with those obtained in the old gravity-mill, the concentrate from which assayed 5.8% copper, 35.5% iron, 37.4% sulphur, 12.7% silica, and 6.5% alumina. The heading ran 2.4% copper, the tailing 1.5%, the

ratio of concentration was 6.6 : 1, and the percentage of recovery of the copper was 50.

At present the tailing normally assays a "trace," which means not over 0.04% copper, a remarkable record, but I believe that any ordinary chalcopyrite ore may be treated by a similar method with similar results. I have myself made a mill-run at this plant with an ore containing 1.38% copper as chalcopyrite, and 22% iron, mostly as pyrrhotite. The grade of the concentrate was 7.32% copper, the tailing 0.07%, the ratio of concentration 5.53 : 1, and the recovery 95.9%. I have in mind two plants operating under license from Minerals Separation, treating simple chalcopyrite ores, that do not contain nearly so much pyrite as the Calaveras ore and therefore should be much easier to concentrate. Each of these plants uses a more complicated flow-sheet than the Copperopolis plant, and is proud of a tailing containing 0.15% copper. This is eloquent evidence concerning benefits accruing to licensees of Minerals Separation from the superior (?) metallurgical knowledge placed at their disposal by that syndicate.

Operating Costs.—These are shown by the following figures taken at random from the company's books, representing actual costs for the week ended July 7, 1916:

Power, 184 hp. per day, at 0.825c. per kw-hr	$191.25
Operating labor, 70 shifts, at $3.25	228.75
Superintendence, repair, and extra labor	137.48
Supplies of all kinds	132.40
	$689.88

On a normal tonnage of 192 per day, this is equivalent to 51.4c. per ton.

Transportation.—Incoming supplies and outgoing concentrate are hauled between Milton and Copperopolis by wagon with trailers, drawn by 14 horses, and carrying about 12 tons per load, at a contract price of $3.25 per ton, or about 20c. per ton-mile. The road is very rough, and attempts to use auto-trucks have resulted in failure thus far. During the rainy season the condition of the road is so bad that it is impossible to do any hauling; it

has been necessary even to suspend operations during that period. Rail-freight on the concentrate is $1.25 per ton from Milton to the smelter on San Francisco bay, and $6.40 per ton to Tacoma, where this product is now shipped.

Future Operations.—There has just been installed an 8-ft. by 30-in. Hardinge ball-mill on trial, under a guarantee by its manufacturer that it will grind 25% more ore, with 25% less power than the 7 by 6-ft. Allis-Chalmers mill. It should be remarked, however, that the price of the Hardinge mill is $1800 more than that of the Allis-Chalmers.

The two ball-mills together, whether operated in series or in parallel, are expected to have a capacity of about 500 tons per day, and 10 additional flotation-cells, with the necessary blower, are being installed to take care of the increased tonnage. The present Oliver filter (8-ft. diam. by 6-ft. face) is to be supplemented by one of the same face but 11½ ft. diameter. This is expected to handle 50 tons per day of thickened concentrate, reducing the moisture to about 12%, with a cake half an inch thick.

It is proposed to convey the concentrate from the thickener to the filter in a 5-in. pipe through the centre of which there will be a 1-in. steam-pipe. This will avoid diluting the thickened concentrate-pulp by condensed steam.

It is estimated that no more labor will be required to operate the plant when treating 500 tons than at present. Assuming the power and supply costs to increase proportionally with the tonnage, an average weekly cost would be approximately as follows:

Power, 479 hp. per day, at 0.825c. per kw-hr	$497
Labor, as at present	366
Supplies	690
	$1553.

This is equivalent to 44.4c. per ton, but it is believed the actual cost will not exceed 40c. On the completion of the railroad, the capacity of the plant may be still further increased by the installation of a third ball-mill, for which room is yet available in the old mill-building.

The total capital expenditure for converting the old gravity-mill into a highly efficient flotation-mill of 500 tons daily capacity will be less than $50,000. A new mill built according to this flow-sheet should not cost much, if any, more, as the figure noted includes the net cost of considerable experimenting, and the dismantling of the entire equipment of the old mill, amounting to as much as a new building would cost under ordinary circumstances.

Without wishing to draw invidious comparisons, it is interesting to note that the National mill in the Cœur d'Alene, built to treat 500 tons per day of a simple chalcopyrite ore, cost $153,000, and has never made so close a saving as the Calaveras plant and cost about the same to operate as the latter with its present small capacity of less than 200 tons per day. Of course, much less was known about flotation when the National mill was built than today.

Messrs. Levy and Trask are modest as to their achievements, but rumors of the excellent results they have accomplished have traveled widely, and the plant has been a Mecca for metallurgists from all parts of the country. Each visitor has departed with a pleasant impression of the courtesy with which he was received and the freedom with which all desired information was made available.

THE DISPOSAL OF FLOTATION PRODUCTS[1]

By Robert S. Lewis

Introduction.—A little over two years ago, I was talking with a millman from a certain plant where the flotation process had recently been introduced. To my inquiry regarding the success of the flotation equipment, he replied that, at first, it was impossible to obtain a froth. Then suddenly, due to some reason not understood, froth began to form so rapidly that it soon ran over the machines and piled up in great heaps on the mill-floor. It was of such a tough and lasting nature that it would have been an excellent substitute for sole-leather, and it was practically impossible to handle the concentrate because of its stickiness. These statements may contain some exaggerations, but they indicated that a mill-operator's troubles might not cease as soon as a froth was produced. Despite the improvements that have been made in the technique of the flotation process, the satisfactory handling and disposal of flotation concentrate is still a very important problem. In order to secure the latest data on the practice of handling flotation concentrate, a number of letters of inquiry were sent to companies operating mills or smelters. Nearly all the information given below is the result of this investigation.

De-watering Flotation Concentrate.—This step is necessary as a preliminary to subsequent handling and metallurgical treatment. The large amount of water present in the froth must be reduced greatly before the concentrate can be transported economically, either in sacks or in bulk, to its destination. If shipped a long distance, the freight-charge on the moisture contained may reach a considerable figure. The expense for un-

[1] From the *Mining and Scientific Press* of April 7, 1917.

loading wet and sticky material from cars is much greater than usual. Then, too, custom-smelters often impose a penalty for moisture in excess of a specified figure. It is interesting to note that steamship companies refuse to carry a flotation concentrate that is very wet. Such materials shift so easily that it is impossible to keep the vessel on an even keel. After one ship had been lost, due to shifting of the cargo, steamship companies refused to transport concentrate in which the moisture ran over a stipulated amount.

When the froth is delicate and breaks easily, as does much of the froth from flotation machines using only air-agitation, a simple treatment on a concentrating-table of the Wilfley type may give satisfactory results. However, it is generally necessary to employ some additional means to insure disintegration of the froth. Centrifugal pumps have been used with success. Bucket-elevators are fairly efficient, but unless included in the original design of a plant, are hardly to be recommended. At the Utah Apex mill, an elevator 71 ft. high is used to assist froth-breaking. Head-room and floor-space may be saved by employing a jet of water instead. Experience has shown that a single large jet, spreading over the full width of the concentrate-launder, is to be preferred to a number of smaller jets. In the Daly-Judge mill, at Park City, Utah, a patent nozzle, known as the Koerting spray, has been found effective in " killing " froth. After passing the spray, the concentrate is thickened in Callow cones and is then treated on Wilfley tables to separate the lead from the zinc. The objection to the use of sprays is that the additional dilution of the concentrate means so much more water to be disposed of later. Moreover, where settling-tanks are employed, any appreciable current in the overflow carries out a considerable amount of the finest concentrate. In an endeavor to overcome this objection, Messrs. Cole and Thompson have devised a special nozzle (U. S. patent 1,180,089, Aug. 18, 1916), in which a gaseous liquid, such as compressed air or steam, is mixed with a small amount of water. The resultant jet has a whirling motion. The spray should be directed against the flow of froth and at an angle of from 60 to 90° with the bottom of the concen-

trate-launder. This retards the progress of the froth and gives the jet more time in which to break it up. The nozzle should be placed at such a distance from the launder as to allow the spray to cover the entire sectional area.

Settling in bins or tanks is a method of de-watering froth that has the merit of simplicity, although it has several disadvantages. Some flotation concentrate is so fine, all −200 mesh and with a large percentage of −300 mesh, that the time required for settling is prohibitively long. Where a large tonnage must be handled the size of the equipment becomes serious. This point is well illustrated in the case of one of the big copper concentrators. An estimate showed that a number of concrete tanks 20 ft. wide, 108 ft. long, and from 5 to 6 ft. deep would be required. The proposed method of operation was to run the froth into a tank until the overflow should become contaminated by the fine concentrate carried over. The tank-feed was then to be cut off and the content settled. The clear water was to be decanted and the concentrate allowed to dry for a day or two. However, the tanks were never built, thickeners and filters being finally adopted. Tanks may have either filter or solid bottoms. In the first case, vacuum-pumps can be used to hasten draining. When solid-bottom tanks are used, the water must be decanted from the settled concentrate, and care must be taken not to allow the escape of the froth, which almost invariably accumulates on the surface of the water. Unless of special design, such as those arranged for a Blaisdell excavator, tanks must be unloaded by shoveling. If desired, the tanks may be provided with steam-pipes to assist drying, but their use is hardly to be recommended. Spreading the material out in a thin layer on a drying-platform gives quicker and better results, but, in any case, drying by steam-heat is expensive. Classifiers of the Ovoca and Akins type have been used for de-watering concentrate. These are quite successful on coarse or granular material that drains readily.

The following examples illustrate the practice of settling flotation concentrate in tanks or bins.

1. The Desloge Consolidated Lead Co., Desloge, Missouri,

has been drying its lead concentrate to 6 or 7% moisture in steel drying-tanks, heated by steam, and then loading it by hand into unlined box-cars. The method is expensive, and the company will soon install a thickener and filter.

2. Monitor Belmont Mining Co., Belmont, Nevada. From 3 to 4 tons of a silicious silver-bearing concentrate is produced per day. The concentrate is settled, drained, and dried on floors to 5% moisture. It is then sacked and hauled to the railroad, where it is loaded into box-cars. The cost per ton for draining and drying is $2.20 and $1.22 for sacking. This method is not satisfactory and the present management is arranging for a totally different method of handling.

3. Name not given. About 45 tons of 60% zinc concentrate, all −65 mesh, is handled daily. The froth, with a water ratio of 6 : 1, is run through a 6-in. pipe into bins. Clear water is drawn off between the settled concentrate and the froth. The bins are of concrete, and each holds 20 tons. They are lined with steam-coils. The dried concentrate, containing about 12% moisture, is dropped through doors in the bottom of the bins into wheelbarrows and is loaded into unlined box-cars. The cost is 40c. per ton for drying and 10c. per ton for loading. Coal costs $2 per ton. The condensation from the pipes is returned to the boilers. A filter will be desirable if a larger tonnage is to be handled.

4. M. W. Atwater, Basin, Montana. About 20 tons of zinc-concentrate is produced daily. All of it is finer than 80 mesh and 70% is greater than 150 mesh. The froth, with a water ratio of 2 : 1, is run into one of four bins, each 10 by 10 ft. and 13 ft. high. The overflow, carrying a small proportion of the concentrate, passes into the next bin. When a bin is filled, the upper three feet is discharged into the overflow-bin. The concentrate is then shoveled through the bin-doors directly into box-cars lined with muslin. Two men can load 80 dry tons in 8 hours. The same men prepare the box-cars for loading and attend to the filling of the bins. The concentrate contains from 12 to 13% moisture when loaded, but this drops to 10 or 12% by the time the smelter is reached. As much as 700 tons of concentrate has been handled in the four

bins in 30 days. The method is satisfactory, but it is necessary to have deep bins and ample bin-space. Cost of loading is 10c. per ton. The lining of the box-cars costs $2 each.

5. Atlas Mining & Milling Co., Sneffels, Colorado. The concentrate assays 10% silica, 20% iron, 12% zinc, 17% lead, 60 oz. silver, and 0.2 oz. gold. Fifteen tons is produced daily. The froth is treated on tables, and the concentrate sent to 50-ton collecting-tanks, the overflow from which is returned to the mill-circuit. From the tanks the concentrate is shoveled into small cars and trammed to an inclined chute 20 in. wide, 18 in. deep, and 90 ft. long, having three steam-pipes along the bottom. The chute discharges into a bin where the concentrate is sacked. It is then hauled to the railroad and shipped in box-cars lined with paper.

6. Mears & Wilfley, Silverton, Colorado. The 10 tons of concentrate made daily is mostly chalcopyrite, and ranges from 80 to 150-mesh. The froth is run into settling-tanks from which two drag-belts, 15 ft. long and 3 ft. wide, requiring ½ hp., pull the concentrate into a bin, from which it is loaded into canvas-lined box-cars by means of wheelbarrows. The concentrate runs 20% moisture when loaded, but only 13% by the time the smelter is reached. The canvas linings are sent back by return-freight. Linings show no wear after six months' use. Cost of handling is about 35c. per ton.

7. Flotation at Mt. Morgan.[2] The ore contains gold, copper pyrite, iron pyrite, and about 70% silica. At the 100-ton testing-plant of this company, the flotation concentrate was first run into round vats 20 ft. in diameter, 10 ft. deep, and constructed with filter-bottoms. These proved unsatisfactory, as the wet slime kept to the outside and did not drain well. This difficulty was finally overcome by using a number of rectangular tanks, 9 ft. 10 in. by 10 ft. 9 in. and 3 ft. deep, with cocoa-matting on a sand-filter bottom. The froth was run through the tanks in series, three or four always being in operation, and each filled with concentrate. The tanks drained to 7 or 8% moisture in 24 hours and the water was perfectly clear.

[2] W. Shellshear, Aust. Inst. M. E., June, 1916.

8. Britannia Mining & Smelting Co.[3] The concentrate, assaying 14% copper, 26.8% iron, and 20.8% silica, is taken from the flotation machines by a drag-elevator that delivers it to the shipment-bins, where the moisture is reduced from 20% to 8% by draining. The Tacoma smelter draws the line at 10% moisture. The overflow from the bins goes to tanks, from which the sediment is delivered to the flotation machines, while the overflow goes to Dorr thickeners. The thickeners give an overflow that goes to waste and a spigot product that is treated in the flotation machines.

At a mill producing 13 tons of concentrate, assaying 5% lead, 5% copper, 28% iron, 18% silica, with some gold and silver, the froth is settled and dried in wooden tanks having steam-coils on the bottom. The concentrate is then shoveled into box-cars that have been lined with paper. Cost is about 18c. for drying, and 23c. for loading, or a total of 41c. per ton. The tanks do not give sufficient settling-area, and the costs are considered high.

At another plant, both a zinc and a lead concentrate are made. The total of concentrates produced is from 3 to 4 tons. The concentrate is settled in shallow tanks, 16 in. and 30 in. deep, the water being decanted. Steam is then turned into pipes on the floor of the tanks. When the moisture is reduced to 11%, the concentrate is shoveled into box-cars lined with resin-sized building-paper. The tanks are housed over. Some are provided with fan-induced draft for drawing off the water-vapor and the rest have natural draft. The former are the more satisfactory. The cost of loading is 21c. per ton.

A plant making 24 tons of lead concentrate per day uses a Dorr thickener to remove most of the water from the froth. The concentrate is then dried to the desired point in tanks 16 in. deep with steam-pipes along the bottom and the sides. Steam-pressure is 75 lb. per sq. in. The concentrate is loaded into unlined box-cars. Cost of treating is $1.15 per ton. The method is not satisfactory, and a filter will soon be installed. This use of steam for reducing the moisture-content of flotation concentrate is expensive.

[3] T. A. Rickard, *M. & S. P.*, Nov. 11, 1916.

In the case of a plant producing 10 tons of concentrate per day, part of which is a 50% zinc product and the rest a 65% lead product, this material is settled in flat-bottom tanks, the water is then decanted, and the concentrate shoveled onto draining-platforms, from which it is loaded into box-cars lined with felt. The zinc concentrate contains 20% moisture, and the lead concentrate 15% moisture. Cost of treatment is about 20c. per ton. This method is only a temporary expedient; thickeners and filter will soon be installed. Even though it could be done easily, it would not be desirable to dry the concentrate to the point of dusting.

It is said that at the Miami mill, the concentrate from both the flotation machines and the tables is run into round steel tanks having filter-bottoms, and with a central opening in the tank-bottom. A vacuum-pump accelerates the draining. When drained, a plug is removed and the concentrate is shoveled onto a belt-conveyor passing beneath the tanks. This conveyor discharges onto another or cross-conveyor that loads directly into box-cars.

The most common method of de-watering flotation concentrate is by the use of thickeners and filters. Though this makes an expensive equipment, it gives a rapid and a fairly positive control over the moisture-content of the finished product. There is some accumulation of froth at the top of the thickeners. This is difficult to handle and contaminates the overflow from the tanks. Unique testimony to the apparent solidity of this accumulation is found at one mill where "near-tragedies" are occasionally enacted because usual canine perspicacity fails to deter inquisitive dogs from attempting to take short cuts across the thickeners. Sprays are sometimes used in an attempt to break up this froth and baffle-boards may be employed, either around the edge of the tanks to protect the overflow, or at the centre and extending below the surface of the water in the tank. In the latter case, the incoming froth discharges into the space within the boards, and is broken up in passing out into the rest of the tank. The Consolidated Arizona Copper Co., at Humboldt, Arizona, has found it profitable to send all the flotation

tailing to thickeners, skim off the froth, and add it to the regular output.

The filters used are generally of the vacuum type, such as the Oliver and Portland, although the Kelly press, a pressure type, has been installed in some mills. The pressure-filter has the advantage that it can reduce the moisture in the concentrate to a very low figure, but it has been considered intermittent in action, costly to operate, and requires close attendance. However, a company that produces a large daily tonnage of concentrate has recently decided to install Kelly filters. These presses, of improved design, were adopted after a competitive test with a filter of the vacuum type. The vacuum-filter has no competitor when treating a concentrate that makes a thick cake and filters easily, but, when the concentrate is exceedingly fine and retains water tenaciously, the capacity of the filter becomes so reduced and the percentage of moisture left in the cake is so high that a filter of the Kelly type is to be preferred. A slight increase in total cost of operation (cost for labor is little, if any, greater than for the vacuum-filter) is more than offset by the reduced moisture in the product. The positive action of the Kelly press enables it to handle material that cannot be satisfactorily treated on a filter of the vacuum type.

In order to give sufficient capacity together with a low proportion of moisture in the cake, the vacuum-filter must have a feed that is at least 50% solid. At one mill the moisture in the material going to the filter must be held at the low figure of 35% in order to get satisfactory results. Heating the pulp in the filter-tank to about 100° F. or adding slaked lime will often increase the capacity of the filter. At the Inspiration mill Dr. Gahl has plotted the percentage of silica in the concentrate along with the moisture-content of the filter-cake. A change in the former due to variations in the ore, or in the operation of the plant, is followed by a closely corresponding change in the latter. This suggests that the percentage of silica present has a marked effect on the de-watering action of the filter. It would be interesting to know whether this holds true in other plants and with different kinds of concentrate.

In a recent bulletin of the American Institute of Mining Engineers, J. M. Callow discusses the continuous thickening of feed for vacuum-filters. He states: "Our experience has not been satisfactory with the continuous plan, and it is for this reason that in all our recent plants, we have been installing the intermittent system. Until shown to the contrary, we think that this offers the best solution, in that with it you have complete control of the necessary density for the filters, there is no danger from losses in the overflow, and the froth which accumulates during the filling of the tank is completely disposed of at each cycle of the operation, and, therefore, cannot accumulate. The agitator for stirring the contents of the tank during the discharge period is copied from those used at the Goldfield Consolidated mill. It consists of arms secured to a square revolving shaft, suspended by a chain-block, and passing through a square hole in the driving-gear. It is simple, inexpensive, and gives no trouble whatever. It is illustrated in the accompanying figure. The thickened pulp may be drawn off from a central-bottom discharge. More recent practice is to draw off through a valve or molasses gate on the side of the tank, or better still, with a diaphragm-pump." Fig. 1 shows an installation for a 60-ton zinc plant.

The following examples illustrate the practice of filtering flotation concentrate.

1. Montezuma Mines & Milling Co., Montezuma, Colorado. This plant is producing daily 10 tons of concentrate that assays 42% zinc and 9% iron. The froth is sent to tables and the table-concentrate is filtered. The cake contains only 3% moisture.

2. Portland Gold Mining Co., Victor, Colorado. From 13 to 15 tons of concentrate, assaying 55 to 70% silica and 2 oz. gold, is made daily. The froth goes to Dorr thickeners and Portland filters. The moisture in the filter-cake is 30%. The concentrate is loaded by hand into tight-bottom box-cars. Cost of de-watering and loading is 50c. per ton. The results are not considered satisfactory.

3. Name omitted. Daily production is 10 tons of concentrate, assaying 40% zinc, 7% silica, 14% iron, 30% sulphur, 7%

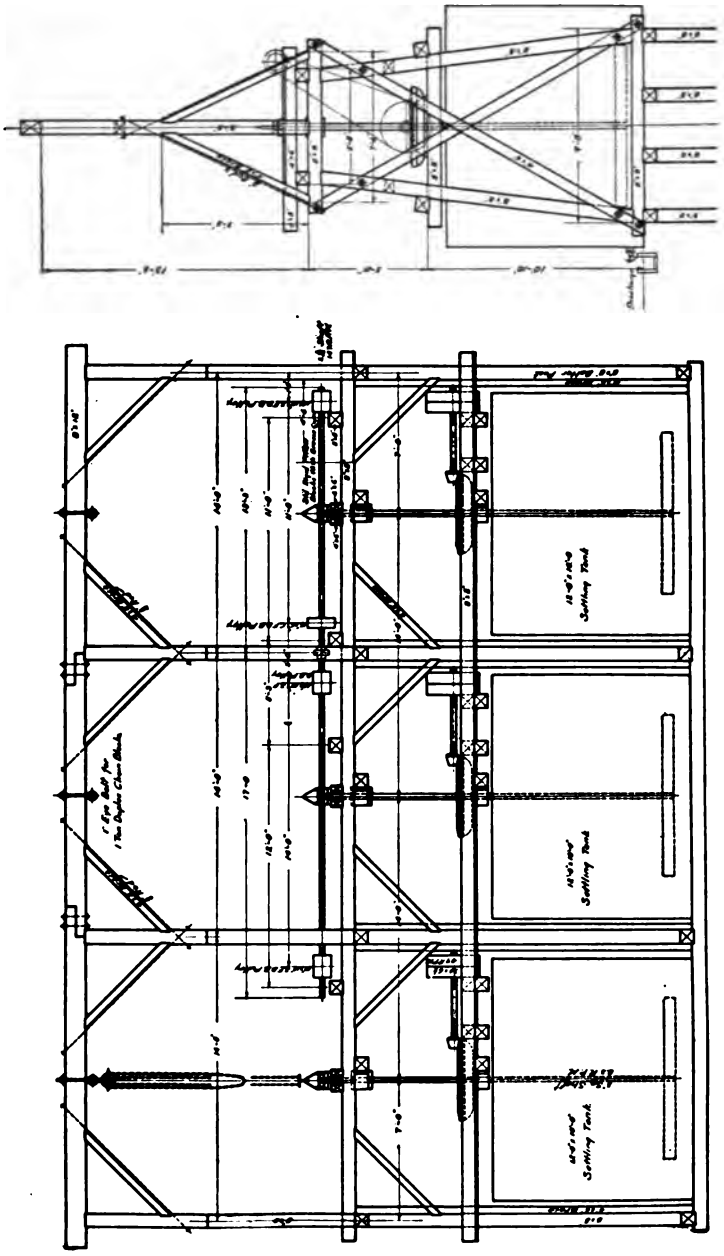


FIG. 1.—Agitators for 12 by 10-ft. Tanks, 50-ton Zinc Plant, Magma Copper Co.

lead, with a little gold, silver, and copper. This is de-watered in Portland filters to 14% moisture, and loaded by hand into unlined box-cars. The cost for de-watering and loading is 15c. per ton.

4. St. Joseph Lead Co., Bonne Terre, Missouri. Forty tons of concentrate is handled per day. The analysis is 50% lead, 2% zinc, 9% lime, 4% iron, and 6% insoluble. The froth, containing 90% moisture, goes to a 38 by 6-ft. Dorr thickener, which gives a spigot-product of 35% moisture. This pulp is sent to one 11 ft. 6 in. by 12-ft. Oliver filter, and the cake, containing 14% moisture, is loaded into gondola cars by means of a rubber-

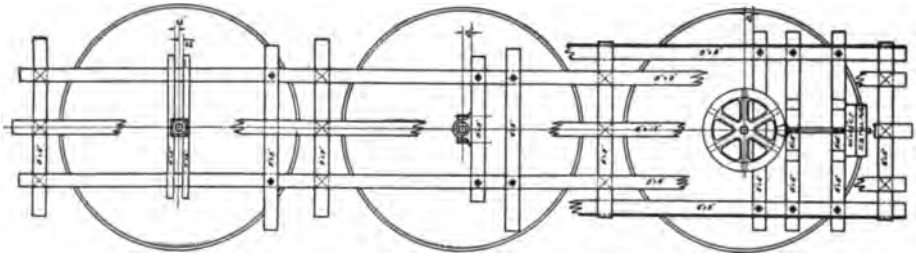


FIG. 2.—Plan of Agitators in Magma Mill.

belt conveyor. A Root vacuum-pump, requiring 29½ hp., is used for the filter. The operation of the filter itself required 1½ hp. Cost for de-watering is 26c., for loading 2c., and for maintenance 6c., making a total of 34c. per ton.

5. Engels Copper Mining Co., Taylorsville, California. Between 30 and 40 tons of concentrate is produced in 16 hours. The assay is 35% copper and 30% insoluble. The froth is elevated to two settling-tanks having cone-shaped bottoms. The thickened concentrate then goes to an 8 by 8-ft. Oliver filter, which gives a cake containing 12% moisture. Steam is used to heat the pulp in the filter-tank. The filter-product is sacked and carried 1½ miles by a tram to auto-trucks, which, in turn, carry the concentrate to the railroad 30 miles away. The cost for de-watering and filtering is $1.50 per ton.

6. Bunker Hill & Sullivan M. & C. Co., Kellogg, Idaho. Analysis of concentrate is 45.9% lead, 6.6% zinc, 13.2% sulphur, 10.4%

insoluble, 9.8% iron, 26.6 oz. silver with a little copper and manganese. Twenty tons is produced per day, all of it −200 mesh. A 40 by 12-ft. Dorr thickener and a 6 by 8-ft. Oliver filter are used for de-watering. The filtered concentrate contains 11% moisture. It is loaded into box-cars. The cost is 7c. for de-watering and 15c. for loading, making a total of 22c. per dry ton. It is essential that the feed to the filter be as thick as possible, about 35% moisture being a satisfactory figure. It has been found that wiping the oily film that forms on the filter-cake, with a rawhide beater, reduces the moisture nearly one-half.

7. Detroit Copper Mining Co., Morenci, Arizona. All flotation concentrate goes to one Dorr thickener. A 6 by 8-ft. Oliver filter takes as much of the thickened product as it can handle, together with the froth from the top of the thickener, which is removed by paddle-wheels. The slime-overflow from the thickener is sent to a settling-tank, and the spigot-product is shipped as flotation slime. An analysis of a composite sample of the filter-product and slime is 20.32% copper, 22.3% silica, 13.2% iron, 12.6% alumina, 1.4% lime, 1% magnesia, and 19.8% sulphur. The moisture in the filtered concentrate is 34.6%, and the slime carries 80.6% moisture, which necessitates its being shipped in tank-cars. The equipment is inadequate, and a larger plant is required to give satisfactory results.

8. Consolidated Nevada-Utah Corporation, Pioche, Nevada. About half of the total tonnage, 18 tons of concentrate per day, is thickened and filtered. It assays 42% zinc, 10% iron, 1% lead, and 11% insoluble. The flotation concentrate is very slimy and is mixed with the fine concentrate from the tables in order to obtain a product that can be filtered satisfactorily. The coarse concentrate from the roughing-tables is not filtered. Three 16-ft. agitators are used for thickening. One is running and one is filling while the third is being decanted. Each requires 5 hp. The 4 by 8-ft. Portland filter reduces the moisture to between 9 and 10% and consumes 1 hp. in operation. The concentrate is shipped in box-cars with a 12-in. board nailed across the door.

9. Old Dominion Copper Mining & Smelting Co., Globe,

Arizona. Of the 36 dry tons of concentrate handled per day, fully 91% is −200 mesh. An analysis gives 18% copper, 24% iron, 27% sulphur, and 22% insoluble. The froth, containing 8% solid, is pumped by a 3-in. centrifugal pump to a 10 by 28-ft. Dorr thickener, which gives a spigot-product of about 57% solid. This goes to an 8 by 11.5-ft. Oliver filter. The filter-cake contains 19% moisture. The filter discharges into a bin from which the concentrate is loaded into cars by means of wheelbarrows. The power consumption of thickener and filter is 1.24 kw. per hour. The filter operates at a 21-in. vacuum and 18 lb. for blowing-pressure. Cost is 1.6c. for de-watering and filter power, 8c. for repairs to filter and renewal of canvas, and 21c. for loading concentrate, making a total of 30.6c. per ton. The comparatively high cost of loading is due to the necessity of loading into box-cars, which makes it impossible to use a belt-conveyor. Trouble is experienced from the accumulation of froth in the thickener. This robs the thickener of settling and thickening capacity. Sprays of water break up some of the froth but do not prevent a gradual accumulation.

10. Utah Leasing Co., Newhouse, Utah. The froth goes to a 22 by 10-ft. Dorr thickener and then to an 8 by 6-ft. Oliver filter, which gives a product containing 20 to 21% moisture. Great difficulty is experienced in settling and filtering the fine slime. Sodium silicate, soda-ash, and lime have been tried, but without marked success. Allowing 24 hours, or more, of undisturbed settling in tanks seemed to be of little avail. Fifteen tons of concentrate is produced daily. It assays 15 to 16% copper, 33 to 36% silica, and 20 to 22% iron.

11. Gold Hunter Mining & Smelting Co., Mullan, Idaho. A screen-analysis of the 30 tons of concentrate produced per day shows the following results: +100 mesh, 0.2%; +150 mesh, 1.8%; +200 mesh, 6.4%; and −200 mesh, 91.6%. It is a lead concentrate with about 16% silica. The froth is thickened to more than 50% solid in a 30 by 5-ft. Dorr thickener. Froth, running 60% solid, is mechanically skimmed at the top of the tank and unites with the spigot-product, going to an 8 by 6-ft. Oliver filter. A vacuum of from 24 to 25 in. is maintained by a

wet-vacuum pump. A receiver with a barometric leg is used for the filtrate, which is clean but is run to settling-tanks. Oakdale No. 3 twill is used for the filter-cover. It lasts six months. The agitator is run at 30 r.p.m., but the air-lifts are not used. The emergency air-agitators are used once daily. The canvas is blown from one to three times per day with compressed air under 20 lb. pressure. Occasionally the canvas is steamed, using a 1-in. pipe perforated every inch with $\frac{1}{16}$-in. holes. Steam-pressure is 60 lb. per square inch. A scraper is mounted on a flat rigid casting that holds it just off the wires. The dried product drops into a bin, from which it is loaded into unlined box-cars by means of wheelbarrows. The concentrate contains 10% moisture. The overflow from the thickener is generally clean, but at times a little froth escapes. The overflow goes to settling-tanks and ponds. The cost is $4\frac{1}{3}$c. for de-watering, of which $3\frac{1}{3}$c. is for power and the rest is for repairs and labor. Loading costs 14c. per ton, being based on a wage of $4.50 for 8 hours. The filtered concentrate takes up more space and this adds to the cost, as it has to be shoveled back into cars.

12. Anaconda Copper Mining Co., Anaconda, Montana. From 1800 to 1900 tons of wet concentrate is produced per day. This is about 148 tons per filter-day. The screen analysis shows +48 mesh, 0.19%; −48 and +200 mesh, 29.7%; −200 and +300 mesh, 11.91%; −300 mesh, 57.18%. The chemical analysis shows 9% copper, 28% silica, 25% iron oxide, 10% alumina, and 27% sulphur. Twenty-one 50 by 12-ft. Dorr thickeners are used. The thickeners for the slime-concentrate require 15 minutes for a revolution and consume 0.6 hp. each. Those for the sand-concentrate revolve once in 9 minutes and consume 1.5 hp. each. The thirteen $11\frac{1}{2}$ by 12-ft. Oliver filters require 1 hp. each for operation, 2.5 hp. each for wet vacuum, and 1.5 hp. each for dry vacuum. The filter-feed is thickened to 50% solid, and the cake runs 15% moisture. The pulp is heated to 100° F. in the filter-tank. The filtered concentrate is taken directly to the roasters on an 18-in. belt-conveyor, which requires 2.5 hp. for its operation. The method is satisfactory. The belt-conveyor handles the material without difficulty. The

froth, containing from 18 to 20% solid, is delivered to a baffle-box at the centre of each Dorr thickener. The box is about 5 ft. square and extends down to within a few inches of the rakes. Surrounding this is another baffle about 15 ft. square and extending about 18 in. below the surface of the water. The baffles catch a large part of the froth, which is there broken up by a spray of water. The overflow, containing a small amount of fine material that will not settle, is run to a slime-pond.

13. Calaveras Copper Co., Copperopolis, California.[4] The concentrate contains 14.4% copper, 29.5% iron, and 14.9% insoluble. When the re-modeling of the plant is completed about 50 tons of concentrate will be produced daily. At present the output is 25 to 28 tons. The froth is thickened to 60% solid in a 22 by 10-ft. Dorr thickener and the moisture is reduced to 13% by means of an 8-ft. Oliver filter. In the new plant, it is planned to convey the thickened product to the filters through a 5-in. pipe, which will contain a 1-in. steam-pipe. This will heat the pulp without diluting it with the condensed steam.

14. Braden Copper Co., Chile. Both the table and flotation concentrates are run into concrete settling-tanks at the bottom of the mill. There are eight tanks in all, and four are used together alternately. The settled-table and coarse-flotation concentrates are loaded by a grab-bucket into cars. The tank-overflow, having a water-ratio of 10 or 20 : 1, goes to Dorr thickeners and the thickened product (water-ratio of 1 : 1), is sent to two Kelly and four Oliver filters, only four of which are in operation at the same time. About 50 tons of solid per day is recovered in this manner. The fineness of the material, 98% of which is −200 mesh, results in low filter-capacity. At this plant supplies constitute 60.4% of the total direct milling-cost. Concentrate-handling makes up 8.33% of the total labor and 1.14% of the total supplies. Filtering concentrate makes up 5.46% of the total labor and 2.61% of the total supplies. About 50 tons is handled per day, of which 98% is −200 mesh.

15. Inspiration Consolidated Copper Co., Miami, Arizona. Five 60-ft. and three 80-ft. Dorr thickeners are used for handling

[4] H. R. Robbins, *M. & S. P.*, Nov. 25, 1916.

651 dry tons per day of mixed table and flotation concentrates. The latter amounts to 75% of total concentrates by weight and carries 90% of the copper. This gives 44.8 sq. ft. settling-area per ton of concentrate. The thickened product, having a water ratio of 1.65 : 1, passes through tunnels to two bucket-elevators, which deliver it to six 11 ft. 6 in. by 12-ft. Oliver filters. The filter-cake contains approximately 17% moisture. In attempting to reduce the moisture in the cake, the pulp in the filter-tanks was heated by steam. This increased the capacity of the filters, but did not affect the moisture in the cake. Adding slaked lime

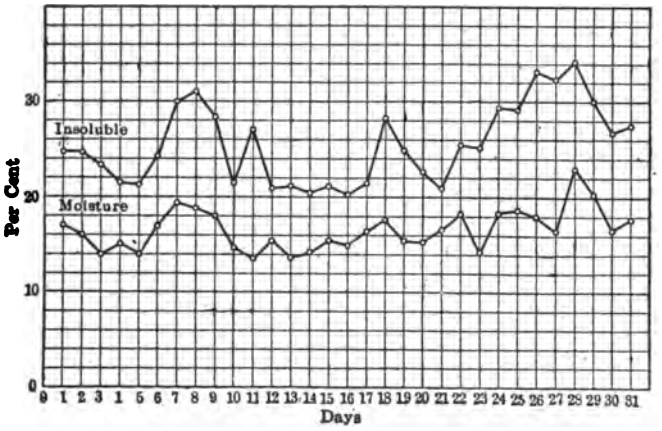


FIG. 3.—Chart Showing Silica in Concentrate and Moisture in Filter-Cake.

gave the same result. Lime is now used to increase the capacity of the filters. A double ring of high boards is used to prevent the contamination of the thickener-overflow by the froth accumulated on top. A record was kept of the portion of silica in the concentrate and the moisture in the filter-cake. The results are shown in the accompanying chart, Fig. 3 (Sept., 1916, Bull., A. I. M. E.), and would seem to indicate that the amount of moisture remaining in the cake depends upon the silica present in the concentrate. An 18-in. belt-conveyor running at a speed of 150 ft. per min. carries the concentrate to a steel loading-bin, directly above the railroad track. At the head pulley a rubber scraper is used to assist in removing the concentrate from the belt-con-

veyor. The bin is round with a cone-shaped bottom. Some difficulty is experienced in discharging the material from the bin. The total power-consumption for thickening, elevating, filtering, and conveying is 5.1 kw-hr. per ton of concentrate. The cost of de-watering and loading is between 20 and 25c. per ton.

A certain plant, producing 15 tons of a 12% copper concentrate per day, uses a Dorr thickener and a 4 by 8-ft. Oliver filter. The cake is shoveled into wagons. Cost for de-watering and loading is given as 50c. per ton. Another plant, making 35 tons of zinc-lead concentrate per day, delivers the froth to a bucket-elevator in order to break it up. It then goes, without de-watering, to an Oliver filter, which gives a cake containing 10% moisture. This is loaded into gondola cars lined with canvas. The cost is 10c. per ton.

A copper company, which produces from 15 to 18 tons of concentrate per day, assaying from 14 to 18% copper and 28 to 34% silica, thickens the froth in Callow cones and then sends it to an Oliver filter. The filter-cake drops down a chute lined with 1.5-in. steam-pipes into a bin, which is also lined with steam-pipes. The concentrate is then shoveled from the bin, and shipped in gondola cars patched with sacks and thin boards. In spite of the filtering and drying, the shipping-concentrate runs from 14 to 18% moisture. It is so wet and sticky that it requires a great deal of shoveling. Cost of loading is from 22 to 25c. per ton. The de-watering and drying cost is not known.

Smelting Flotation Concentrate.—The concentrate generally comes to smelters so well established in methods of operation that their work is of a routine nature. If this material is put through the regular smelting process, it has been found that the physical condition of the concentrate is such as to require certain modifications in the usual methods of operation.

The actual smelting of a flotation product is quite similar to the smelting of any other concentrate. The objections to it are of a physical rather than of a chemical nature, but they are enough to cause many smelters to impose a penalty of $1 per ton. If the concentrate arrives at the smelter in a wet and sticky condition, it is difficult and expensive to unload. A large mois-

ture-content means extra fuel-consumption in driers and roasters, and in furnaces, when charged directly into them. The great fineness of the material causes a heavy loss from dusting. This is especially true where it is necessary to smelt in blast-furnaces. Briquetting should reduce this loss, but it is often difficult to produce satisfactory briquettes. Unless it can be mixed with a large proportion of coarse material, flotation concentrate is hard to sinter. It chokes the grates, interferes with the draft, and reduces the capacity of the sintering-machines. In some cases it may be necessary to pre-roast before a successful sinter can be produced. During the roasting process, there is often a marked

FIG. 4.—Lumps of Incompletely Roasted Zinc Concentrate Showing Unaltered Cores of Sulphide.

tendency toward agglomeration or " balling up," and lumps are formed that roast on the outside only. Fig. 4 shows two lumps (natural size) of zinc concentrate that passed through the roaster, but came out with unaltered cores. Often troublesome accretions are formed in the roasters. At one plant it was found that a preliminary drying of the concentrate before roasting prevented " balling." However, drying usually makes the material lumpy and hard to feed. Where a large amount of flotation concentrate is roasted, special apron-feeders must be provided to handle this material.

The roasted product is of such a light and fluffy nature tha it must be handled with great care to keep down the loss from

dusting. At one plant, the cars are loaded in a tunnel connected to a dust-chamber and stack. Should a sufficiently large amount of dust be produced, it would pay to add a Cottrell tube-system. At another copper smelter, the side walls of the reverberatory furnaces have slots cut through them just above the slag-line. Inclined iron plates are fastened to the outside of the walls so that the charge can be shoveled onto them and work slowly down into the furnace as the smelting proceeds. This method of gently presenting the charge to the heat at a point where the draft is weakest causes a minimum formation of dust. It is far less than if centre-charging is used.

The foregoing discussion concerns lead and copper smelting, but zinc smelters, as well, have their troubles when treating flotation concentrate. At one plant, the unloading from cars is done by shoveling or by a grab-bucket. The material is then dried in a rotary drier and roasted in muffle-kilns. Because of its fineness, it is considered more difficult to treat than other zinc concentrate. At a second plant, all the unloading is done by shoveling, but it is considered an unsatisfactory method. At a third plant, shoveling is considered expensive, though it is acceptable in other regards. The concentrate is roasted in open-hearth furnaces fired with natural gas. Very little trouble is experienced in roasting. No difficulty is found in smelting, but the dust-loss is higher than for coarser material. At a fourth plant, flotation concentrate makes trouble all through the smelting process. Unloading is done by shoveling into wheelbarrows. The material is frozen in winter and is hard to handle. It is roasted in reverberatory furnaces to 1% sulphur or less (cost of roasting is about $1.70 per ton). The coarse concentrate is first dried to about 4% moisture, but the fine concentrate is not dried. The difficulties found in roasting are high dust-loss, the forming of accretions in the roasters, and the fusing of the fine concentrate. Smelting is done in the usual gas-fired distillation-furnaces. The fine material is more subject to loss through overheating. It slags more easily with consequent loss of retorts. The charge is more likely to cake in the charge-cars, if too wet, and to blow out of the retorts,

if too dry. The very fine flotation concentrate is difficult to roast and smelt.

One smelter superintendent forcibly summarizes the situation in the following brief sentence: "Flotation concentrate is considered a damned nuisance."

Examples of smelting practice are given below.

1. Consolidated Mining & Smelting Co. of Canada, Trail, B. C. The amount of flotation concentrate smelted is too small to afford reliable data. It is charged directly into blast-furnaces, so that the dust-loss probably is serious. A briquetting plant is being installed.

2. Omaha Plant, American Smelting & Refining Co., Nebraska. The copper concentrate, used incidentally to supply sulphur to the charge, is briquetted with 7% lime, and, after drying for 72 hours, is charged into the blast-furnaces. This material, even after briquetting, produces considerable flue-dust.

3. U. S. Smelting Co., Midvale, Utah. The concentrate is shoveled from the cars and is briquetted with flue or bag-house dust, heavy with lime that had been introduced for the purpose of neutralization. The cost is about $1 per ton. The sintering in Dwight-Lloyd machines is not good, due to a poor mixing. The product is smelted in lead blast-furnaces. Flotation concentrate is considered a great nuisance.

4. Garfield Smelting Co., Garfield, Utah. The flotation concentrate is mixed with table and vanner products. It is then bedded with fluxing ores and later fed to McDougall and Herreshoff roasters. While the quantity of flotation concentrate treated is too small to cause any serious difficulty or to require special treatment, close observation shows that it has a tendency to form lumps that do not break up easily in the roasters. In fact, some lumps roast only on the outside. A large increase in the amount of flotation concentrate handled would probably necessitate a special feeding device.

5. Selby Smelting Co., California. The flotation concentrate is unloaded by shoveling and is spread out to dry. Cost for spreading is about 30c. per ton. It is then sintered and

smelted in lead blast-furnaces. No trouble is experienced, other than the production of a large amount of flue-dust.

6. Anaconda Copper Mining Co., Montana. About 20% of fine table and jig concentrate is mixed with the flotation product. This is delivered to Wedge roasters by belt-conveyors. Each furnace-bin holds 25 tons. A large steel apron-feeder is used for supplying the material to the furnace. The roasted product is extremely fine and difficult to handle. It is loaded into covered cars in a tunnel that is entirely closed except for a stack at one end, which produces a slight draft. The amount of dust issuing from the stack is small. If sufficiently valuable, the dust could be recovered by a Cottrell precipitator. The smelting in coal-fired reverberatory furnaces presents no difficulties.

7. Murray Plant, American Smelting & Refining Co., Utah. The flotation concentrate arriving at this plant is wet and sticky, and bad to handle. It is mixed with sulphide ores and roasted or sintered and then smelted in lead blast-furnaces. It is considered to have an adverse effect on the smelting process. It chokes the roasters and tends to give a poorly-roasted product. The dust-loss is heavy. The fine powdery product is objectionable from a lead-smelting standpoint.

8. Ohio & Colorado Smelting & Refining Co. All flotation concentrate is either pre-roasted and sintered or sintered directly. The pre-roasting is done, after mixing with coarser material, in Godfrey and Wedge furnaces. The flue-dust and mechanical dust-loss is increased. Dwight-Lloyd machines are used for sintering. Even though coarser material is added, the capacity of the sintering-machines is decreased.

9. Bartlesville Zinc Co., Bartlesville, Oklahoma. The zinc concentrate from filter-presses is unloaded by shoveling. It must be dried in a machine of special design to avoid excessive dust-loss. It is then roasted in ordinary kilns. Allowance for excessive dust-losses met with at every step in its treatment should be provided for when purchasing flotation concentrate.

10. Braden Copper Co., Chile.[5] The first flotation concen-

[5] R. E. Douglass and B. T. Colley, *Eng. & Min. Jour.*, February 12, 1916.

trate produced at the plant was so wet that it could not be briquetted and so fine that it was hard to filter and dry. When charged directly into the blast-furnaces, the amount of coke required was increased from 12 to 16%. The drained concentrate from the bins contained 50% moisture and the filtered concentrate ran 30% moisture. After much experimenting, it was found that nodulizing in rotating kilns gave a product that was a first-class smelting material.

11. International Smelting Co., Miami, Arizona. The concentrate is unloaded from steel cars, having removable bottoms, onto belt-conveyors that deliver it to bedding-bins, where the necessary fluxes are added. The beds contain about 4000 tons, 80% of which is flotation concentrate, and are made in V-shaped steel bins that have removable-slat bottoms. Beginning at one end, the mixture is fed from an approximately vertical face onto a belt-conveyor, which discharges into Wedge roasters, used as driers only. The material is sticky and hard to handle. It is dried to about 14% moisture, and is then fed to oil-fired reverberatory furnaces. The difficulties in smelting are practically of a mechanical nature, due to the handling of this extremely fine charge, 50% of which is −200 mesh. The plant was designed for smelting flotation concentrate, and every precaution was taken to avoid dust-losses.

12. At Mt. Morgan, Queensland, Australia,[6] an ore containing about 2% copper and from $5 to $7 in gold is treated by flotation. Nearly 70% of the gold is free. It was found that by grinding the ore very fine, much of the gold was caught in the thick froth of the flotation machine. The ore was ground to 80-mesh. There was no increase in the saving of copper, but the extra gold recovered paid for the cost of grinding. As long as only a small tonnage was treated, the concentrate was mixed with blast-furnace flue-dust, in the proportion of 1 : 3, and sintered in a Dwight–Lloyd machine with excellent results. But when the percentage of concentrate was increased, the sulphur content rose to such a figure that the machine did not give a good product,

[6] B. Magnus, "Sintering Flotation Concentrates," *Eng. & Min. Jour.*, June 10, 1916.

and its capacity was reduced, owing to the choking of the bed by fine concentrate. Pre-roasting followed by pot-roasting was then tried. An Edwards furnace was first used, but the roasted product was so fine that it could not be handled in the Dwight–Lloyd machine or in the pots. Tests made by pre-roasting in a Godfrey furnace and sintering in pots proved satisfactory, and such a plant was installed. It was found that the product from the Godfrey furnace was coarser than the concentrate, some agglomeration evidently taking place. A sketch of one of the sintering-pots is shown in the accompanying figure.

13. Tacoma Smelting Co., Tacoma, Washington. The flotation concentrate arriving at this plant is unloaded from ships in tubs that are filled by hand-shoveling. Owing to the sticky character of the material, this work is disagreeable and costly. Roasting is done in Herreshoff furnaces, the upper floors of which are used for drying only. It is necessary to clean the roasters frequently. Reverberatory furnaces are used for smelting. Elaborate machinery must be used in order to keep dust-losses from becoming excessive.

14. Helena (Montana) plant of A. S. & R. Co.. Unless filtering or drying has been done at the mill, the flotation concentrate sent to this plant carries from 20 to 25% moisture. In summer this material has the consistence of liquid mud, and could almost be unloaded from cars by means of a pump. In practice, men wearing high rubber boots shovel the concentrate from the cars into bins. The cars can be washed out, but the material sticks to the sides of the bins, dries, and causes loss from dusting. In winter the concentrate will freeze solid in the car, and has to be thawed or else mined with gads and picks. The cost of unloading is then excessive. No particular difficulty is presented when the concentrate has been dried or filtered before shipping. The lead concentrate is first sintered in Dwight–Lloyd machines. From 10 to 15% of flotation concentrate is mixed with miscellaneous sulphide ores, including a small quantity of matte and from 5 to 10% of crushed limestone. With this mixture a fairly good sinter can be obtained. This material is then transferred to H. & H. pots, where it is converted into a slagged and fairly

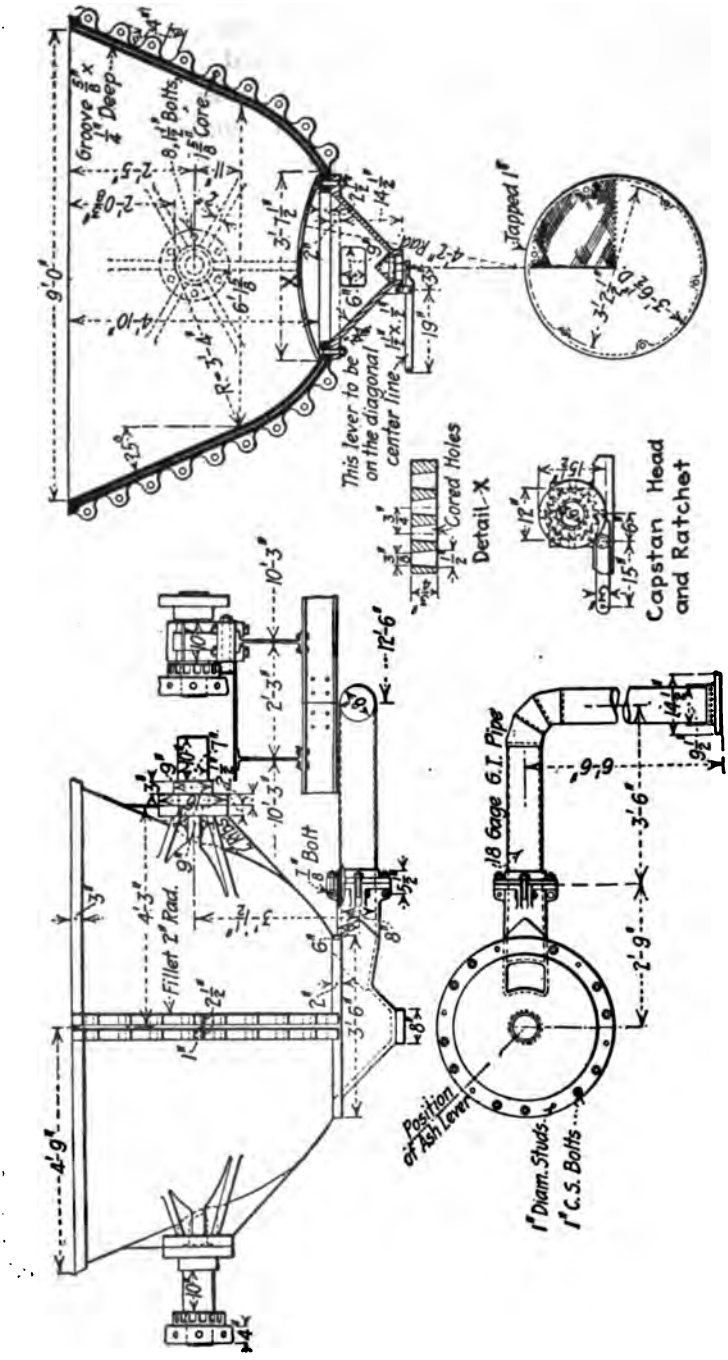


FIG. 5.—Sintering-Pot Used at Mount Morgan.

porous product containing less than 2% sulphur. Smelting in lead blast-furnaces presents no difficulties. Owing to its extreme fineness, smelters must necessarily suffer considerable loss from dusting when handling flotation concentrate. This loss is undoubtedly higher than in the case of ordinary ores or coarse concentrate; therefore it justifies a higher charge for treatment.

Summary.—The various methods of handling froth may be classified as follows:

1. Breaking by means of centrifugal pumps, bucket-elevators, jets, or on tables.
2. De-watering in tanks, with or without filter-bottoms. Steam may be used to assist drying.
3. De-watering in classifiers of the Ovoca and Akins type.
4. Continuous thickening, followed by filtering.
5. Intermittent thickening, followed by filtering.

The use of tanks for de-watering concentrate necessitates unloading by shoveling, unless the tonnage to be handled is sufficiently great to warrant the installation of a crane and grab-bucket. The cost of loading varies from 10c. per ton, where the concentrate can be shoveled directly into cars, to 25c. and more per ton, where wheelbarrows must be used. In case gondola cars are to be loaded, a belt-conveyor will reduce the cost to 2 or 3c. per ton. The employment of steam for drying can hardly be recommended, especially where pipes are placed in tanks. The concentrate should be spread out in a thin layer on a uniformly heated surface. In a tank the concentrate in contact with the steam-pipes is quickly dried, but the moisture is driven out only to condense in the main body of the concentrate, which dries very slowly. Such a method of de-watering is necessarily expensive. Filter-bottoms for tanks may be advisable where the concentrate drains fairly well, and, in such instances, the trouble from accumulated froth is eliminated. Where the water must be decanted from settled concentrate, the decanting apparatus should be so designed that it can work in the clear water between the unbroken floating froth and the top of the settled concentrate.

Continuous thickening, followed by filtering, is a method,

commonly employed, but the troubles arising from the accumulation of floating froth in the thickener and the difficulty, at times experienced, in getting a spigot product low enough in moisture for satisfactory filtering should be considered when making such an installation. One large company gives the cost of thickening in Dorr thickeners, de-watering on a continuous filter, and loading by gravity at 65c. per ton. Another company states that thickening and filtering (continuous type) costs 10c. per ton. Intermittent thickening, followed by filtering, seems to offer the most positive control over the moisture in flotation concentrate. Filters of the pressure type will give good results on material that cannot be satisfactorily treated on vacuum-filters.

A preliminary treatment, before smelting, is nearly always given flotation concentrate. Such treatment would come under one of the following heads, although two or more may be combined:

1. Drying.
2. Briquetting.
3. Nodulizing.
4. Sintering.
5. Roasting.

The difficulties in the smelting of flotation concentrate are caused by the extreme fineness of this material. Briquetting should be a good method of preparing the concentrate for direct smelting in blast-furnaces, but it is not easy to make a strong briquette that will not break up and produce much flue-dust before it is smelted. Nodulizing gives an excellent smelting product, besides driving off some sulphur, but the loss in dust may be considerable. Roasting presents such troubles as the necessity of specially designed feeders for furnaces, the formation of accretions, and the non-roasting of the interior of lumps, heavy dust-losses, and the production of a light fluffy product that is not easy to handle. The cake from sintering or pre-roasting and sintering is quite suitable for feeding to blast-furnaces, but it is necessary to mix coarse material with the flotation concentrate in order to get a well-sintered product and

to prevent too great a falling off in the capacity of the machines.

At the present time flotation concentrate, being a new and unusual material, is difficult to handle. Unless specially designed for the purpose, smelters cannot be expected to treat this product in the smooth manner of their regular work. However, metallurgists are keenly interested in solving the problems thus presented, and, as the tonnage of ores that are being concentrated by the flotation process increases, plants smelting only such concentrate will soon experience no serious hindrance to satisfactory operation.

MECHANICAL DEVELOPMENT IN FLOTATION

By O. C. Ralston

The greater number of inventions that have appeared in connection with flotation during recent years have been of a mechanical nature. Many of them have been mistaken by the uninitiated as belonging to new processes but usually they are only old ideas in a slightly changed form. The more ordinary types of such machines have often been described in the technical press and so will be omitted from this discussion or only briefly mentioned. Many of them are true improvements in the art and many are crude modifications of a good fundamental type designed to avoid infringement.

Mechanical Froth-Making Machines.—In froth-flotation there are many ways of introducing gas into the pulp; one of the oldest and best is to beat air into the pulp by the use of rapidly revolving propellers.

Hoover's book gives drawings of many of the earlier types of machines. These have been used so often in later papers by different writers that they need not be described here. Only the present standard single-level M. S. machine need be shown. See Figs. 1 and 2. This also has been described often. The only thing to be mentioned here is that the gears on the drive-shaft are so set that alternate ones drive the impeller-shafts in opposite directions in order that the thrust on the drive-shaft will be zero—an important point in design. The drive-motors are usually placed at the head of the machine unless hot pulp is being used or acids are being added, in which case the motors are placed at the other end of the machine, so as to avoid steam and corrosive vapors. Fig. 1 shows two standard machines placed back to back in order to economize floor-space. The result of this method

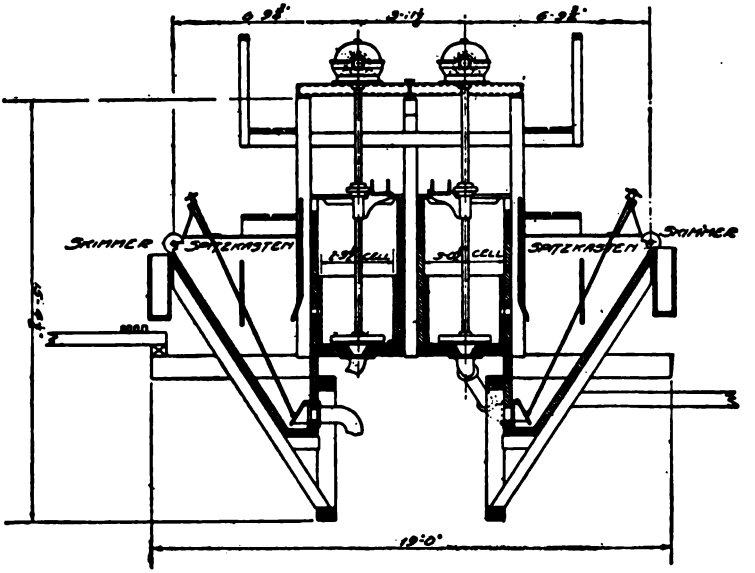


FIG. 1.—Standard M. S. Machines Placed Back to Back.

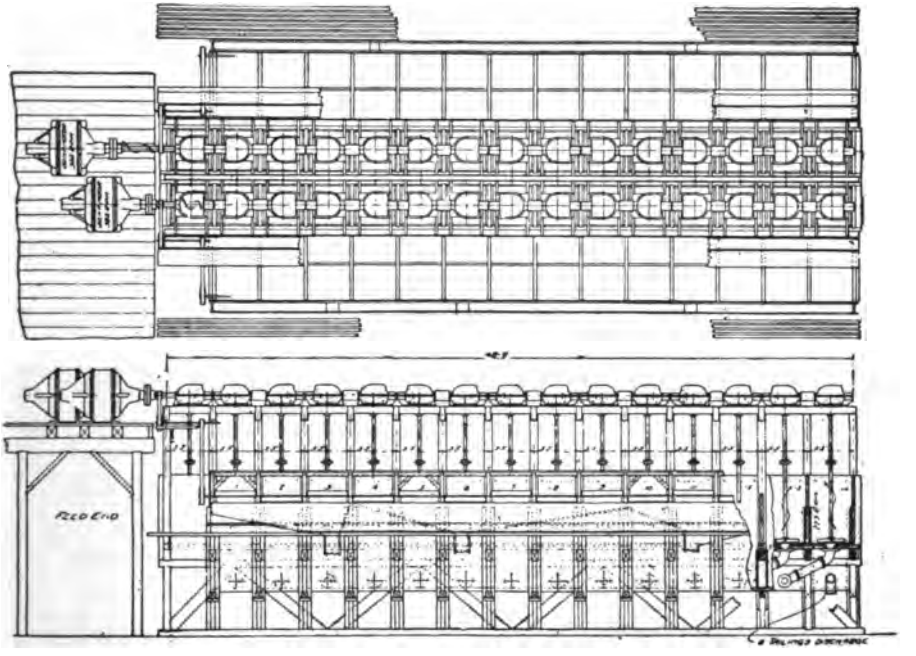


FIG. 2.—Standard Single-Level M. S. Machines.

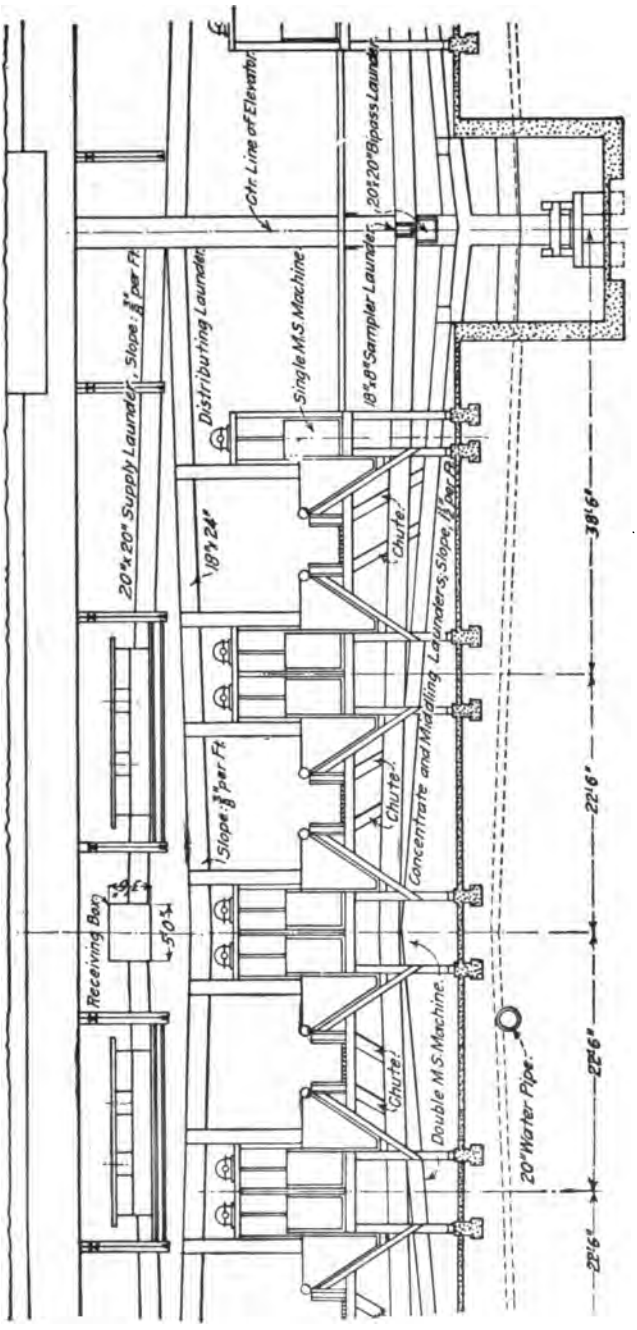


FIG. 3.—Longitudinal Section of Slime-Flotation Plant at Anaconda.

of placing the machines and the method of conducting away the concentrate in launders is indicated in Fig. 3, which shows the longitudinal section of the slime-flotation plant at Anaconda.

By making the impeller-shaft horizontal and turning the blades in a vertical plane, G. B. Eberenz and J. I. Brown, of Cripple Creek, claim a new invention. Their machine is shown in Fig. 4, which is taken from their patent (U. S. 1,187,822 of June 20, 1916). The patentees make the following claims: The blades revolving in a vertical plane can beat air into the

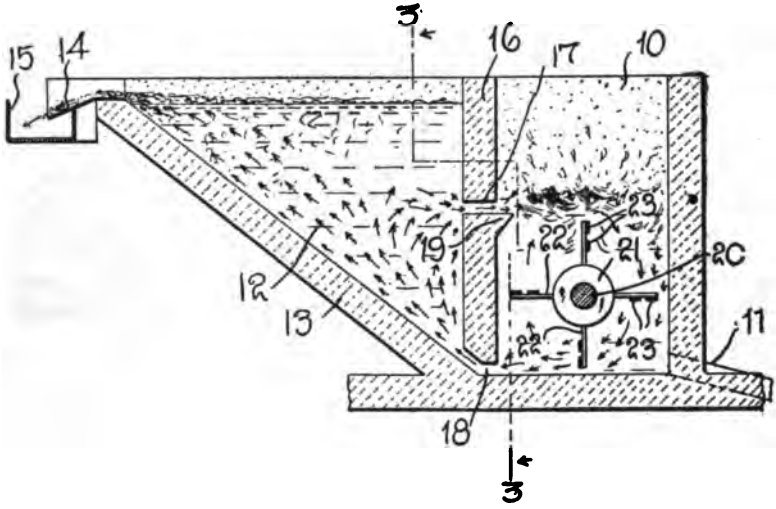


FIG. 4.—Eberenz & Brown Machine.

pulp more effectively. The pulp is driven down into the bottom of the spitzkasten instead of into the side, as is usual in the Minerals Separation machine. A better churning-in of the oil and air is claimed and it is stated that in practical operation the machine makes so much froth through the action of the agitators that no frothing-oil is necessary.

Charles E. Rork, of Douglas, Arizona, invented a machine that was tested in several of the mills of the Phelps Dodge company, notably the Burro Mountain plant at Tyrone, New Mexico. It was patented on April 20, 1915, and the patent-drawings are shown in Fig. 5, as taken from U. S. 1,136,485. By comparing

the figures it can be seen that in the machine of Eberenz & Brown the shaft passes through the end wall of the machine beneath the level of the pulp while in Rork's machine the shaft is above the level of the pulp and hence not subject to continual abrasion, leakage, etc. The paddles merely dip into the pulp and throw it into the top of the beating-chamber. The advantages of having only one rotating shaft are obvious, and if there were no

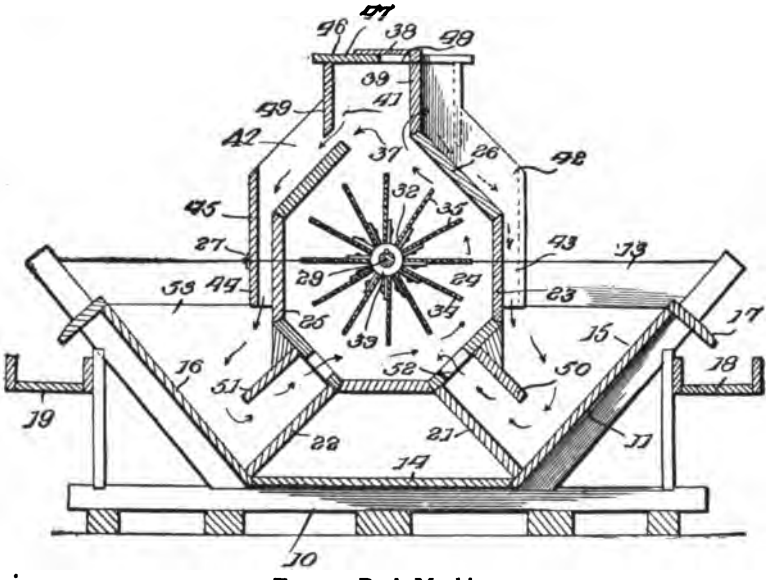


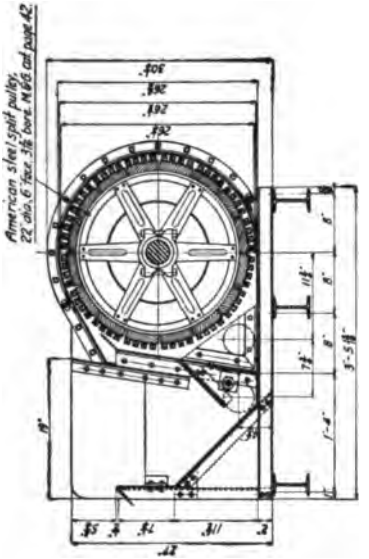
FIG. 5.—Rork Machine.

other advantages over an M. S. machine one might expect this machine to have lower maintenance costs. However, a disadvantage has been discovered in having such a long shaft supporting beating-blades in three or four successive compartments. This shaft is likely to whip unless it is of rather large diameter. Thus the length of the machine is limited. In the tests at Tyrone, Rork's machine was found to use more power than had been expected. On that account modifications of the machine were made until it finally resulted in the form shown below. This is now known and sold as the K. & K. machine, named after the inventors, Max Kraut and F. B. Kollberg, both of Douglas, Arizona.

By expanding Rork's shaft and beaters into a cylindrical drum with a riffled surface, as seen in Fig. 6, considerable longitudinal strength was gained and it was found that the power-consumption was considerably lowered. The whirling cylinder dips into the pulp and the air is trapped between the riffles. The moving part is almost perfectly balanced and the weight of entrained pulp is relatively small. The low consumption of power is a natural consequence of this design and raises the question whether other machines do not whirl all of the pulp to their disadvantage. While the pulp is passing around with the cylinder of the K. & K. machine the centrifugal force is tending to drive it out, so that it receives a considerable aeration in a single revolution of the cylinder and is thrown through the air at the top, to drop into the frothing-spitzkastens. These are four in number.

This machine retains all of the advantages and eliminates some of the troubles of the Rork. The claim is made that it requires no blowers, no compressed air, and no pre-agitators. As far as pre-agitators are concerned, I believe that any machine can do better and faster work if the oil is already well disseminated in the pulp when it reaches the flotation-machine. Otherwise, the machine is extremely simple and requires only a single belt-and-pulley connection to a source of power. The inventors claim a capacity of 80 to 150 tons per 24 hours with 10 to 15 horse-power. These figures seem low and have caused many engineers to doubt their reliability. The fact that these machines are used in nearly all of the mills of the Phelps Dodge companies would indicate that they must have decided merit. The lively appearance of the froth is very attractive. I am inclined to suspect that with low-grade ores these machines would not give as low a tailing as other machines, although they are known to make a high-grade concentrate; therefore it seems advisable to supplement them by pneumatic machines, to glean the tailing.

The Janney machines are of two types; the mechanical and the mechanical-air cells. Both are used in large numbers in some of the largest copper-concentrating mills. They are the invention of T. A. Janney, mill-superintendent for the Utah Copper Company.



K. & K. Machine. Cross-Section.

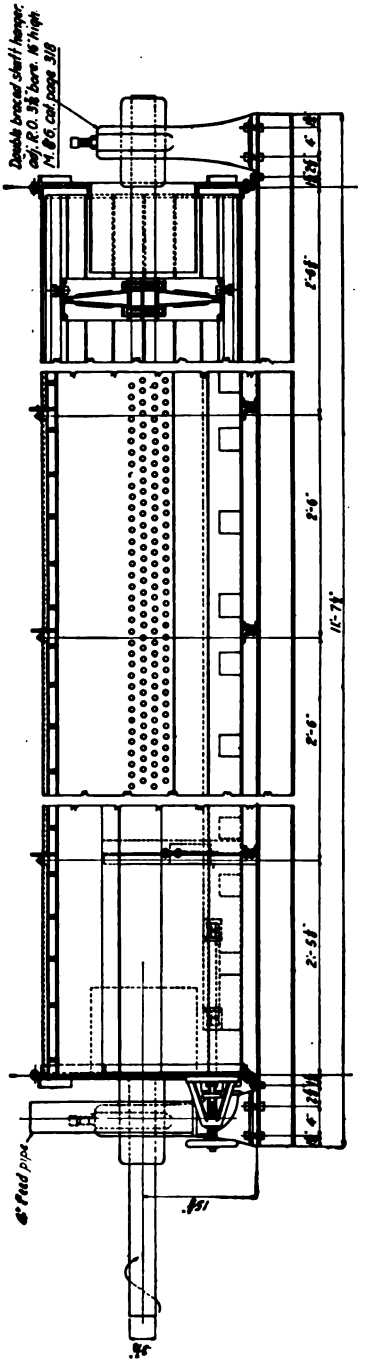


FIG. 6.—K. & K. Machine. Longitudinal Section.

The " mechanical " machine is shown in Fig. 7. This shows that two impellers are used on the same shaft and that the pulp is agitated violently against baffles, which are part of a cast-iron liner. The whirling of the pulp over the top of the liner allows it to flow into the spitzkastens, of which there are two for each agitation-chamber. The agitator-shaft is a continuation of the motor-shaft, being screwed into it, and revolves with the motor at about 570 r.p.m. The first machines were made of one main casting into which fitted replaceable liners, but at the present time concrete is being used for the main portion of the machine and cast liners are used to protect all portions subjected to wear. The drawing shows two circulating pipes, used in each " spitz," up which the pulp passes to the agitation-chamber, the head of pulp in the " spitz " being such that the pulp enters by these pipes to replace the pulp thrown out of the agitation-compartment. Adjustable gates between the adjacent spitzkastens allow the pulp to pass from one cell to the next by gravity. However, the circulating-pipes permit the repeated treatment of most of the pulp in each cell before it passes to the next one. The drawing also shows a good design of a froth-remover which allows any depth or length of stroke.

Since these cells are separately constructed they can be installed in a variety of ways to suit the convenience of the designer. Fig. 8 shows part of an equipment of two mixers and 15 cells in a row. The feed is split between the first five cells. These make clean froth. The tailing then passes in series through the remaining cells, which make middling. This is called the " multiple-series " arrangement. The machine is especially adapted to the flotation of coarse material such as low-grade concentrate produced by vanners and the like. The percentage of solid in such feed should range between 20 and 23. The motors use about 10 hp. each, consequently an installation of this type of machine requires more power than almost any other standard device used for flotation. On that account, the later " mechanical-air " cell has displaced it to a great extent.

The mechanical-air cell, as shown in Fig. 8, likewise utilizes a vertical-shaft motor set directly over the agitation-compart-

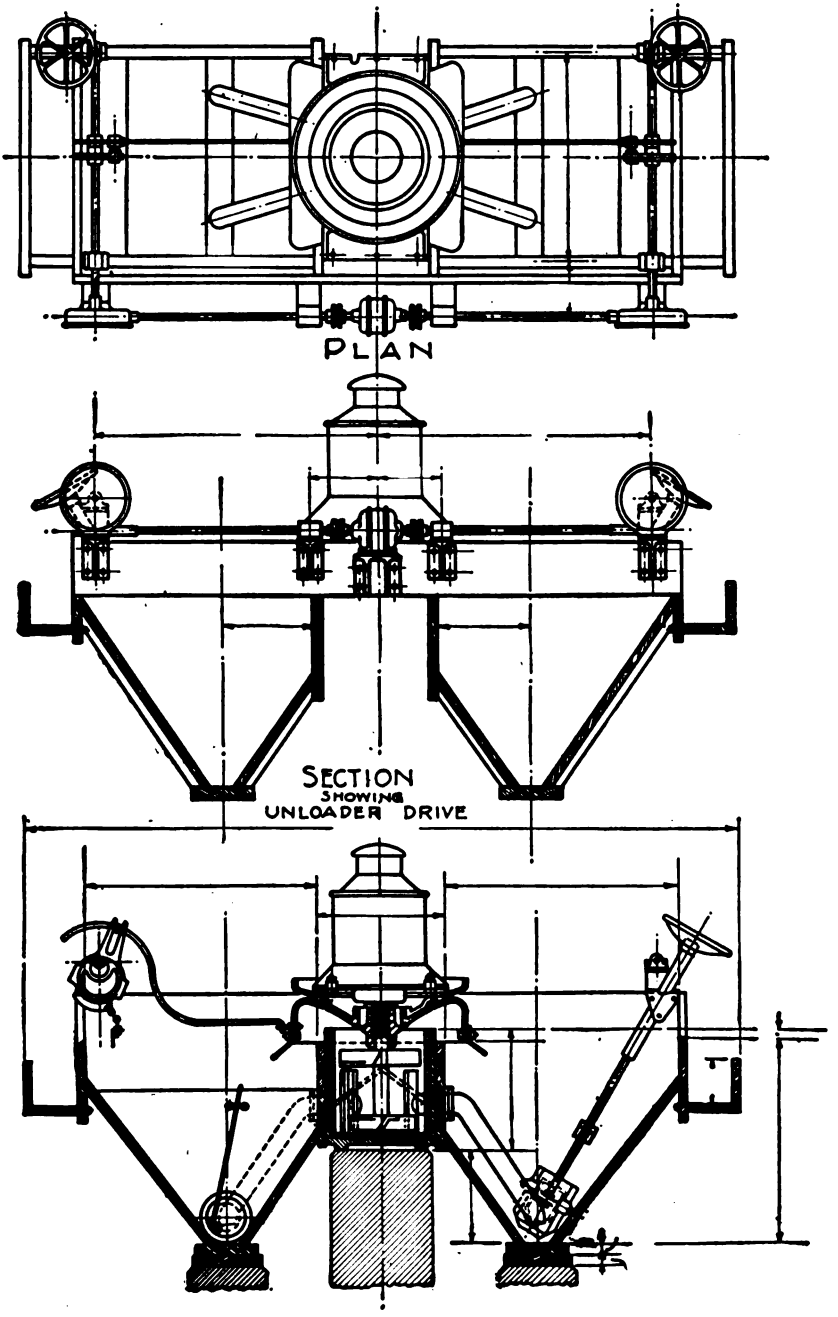


FIG. 7.—Janney Machine.

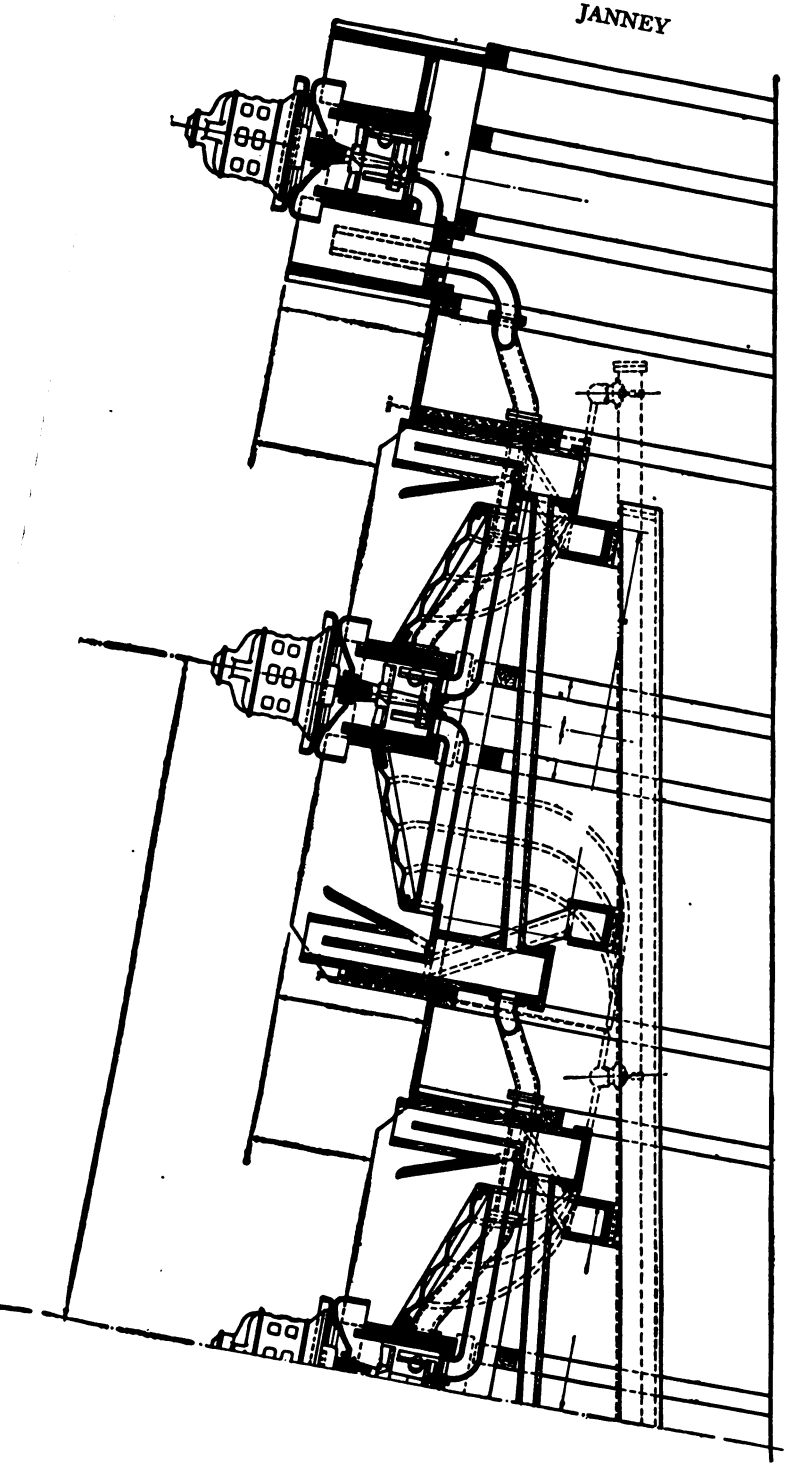


FIG. 8.—Janney Air-Machine.

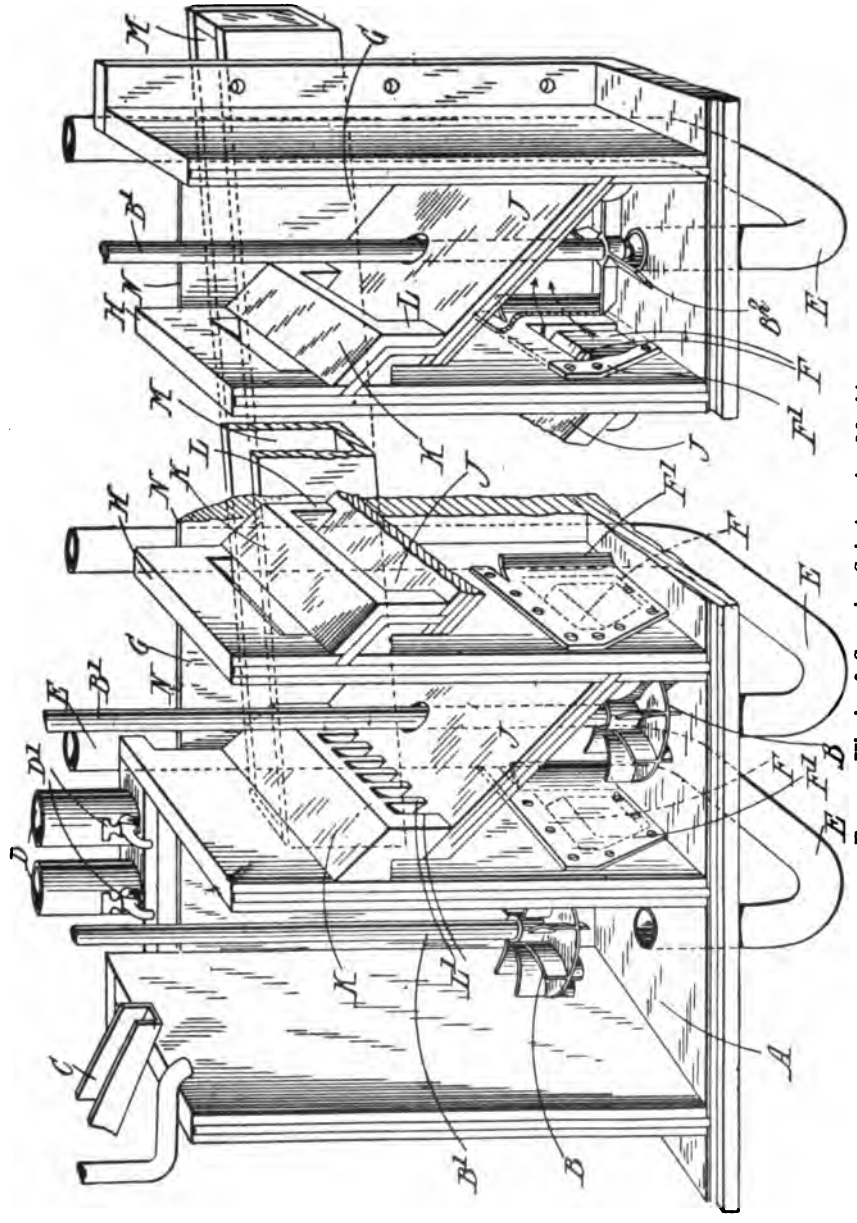


FIG. 9.—Higgins & Stenning Sub-Aeration Machine.

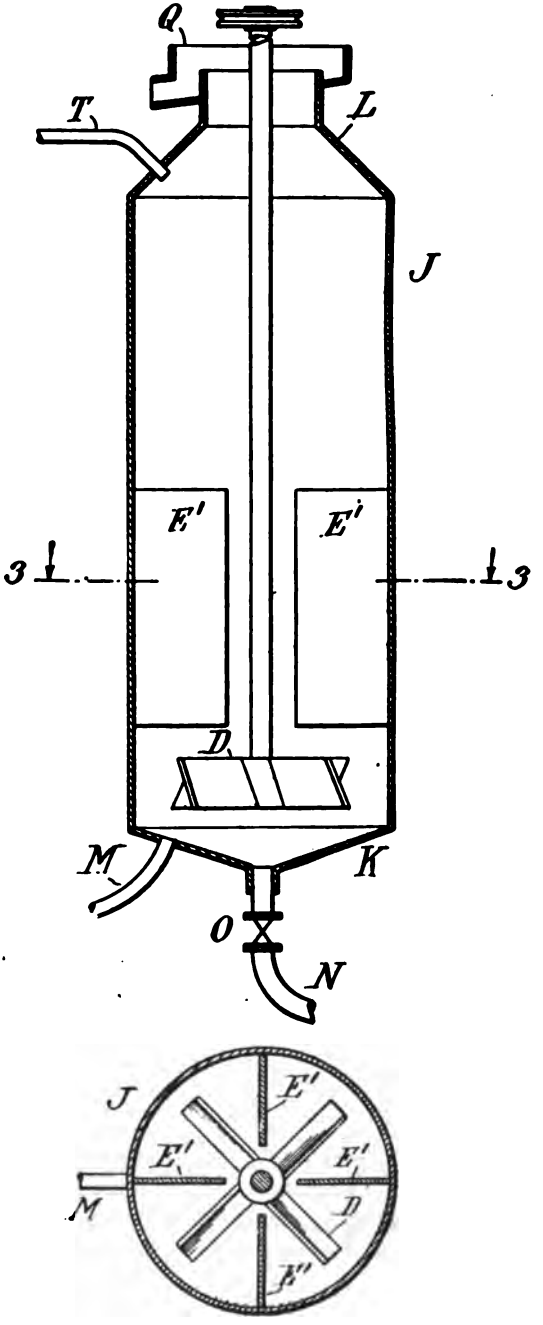


FIG. 10.—The Owen Machine.

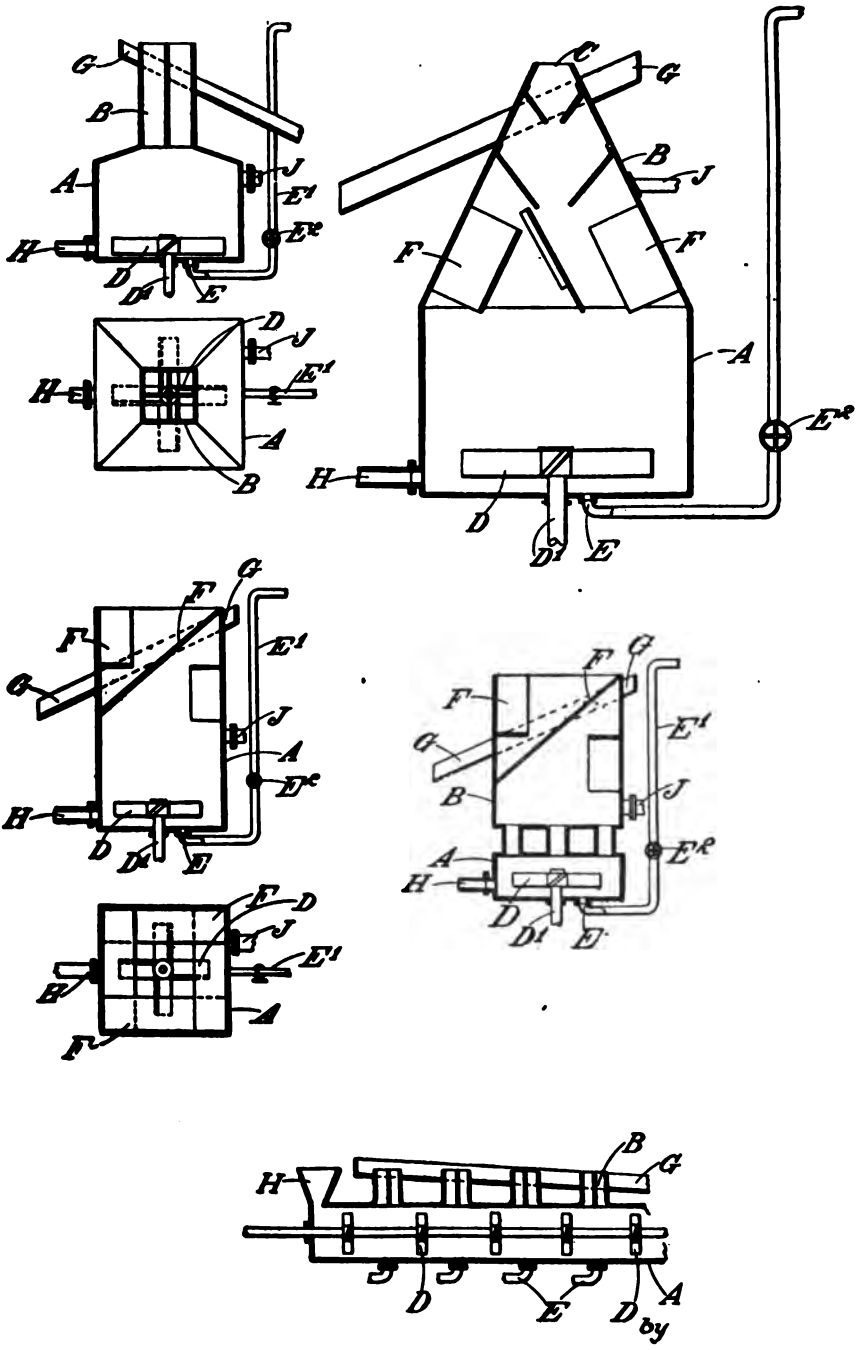


FIG. 11.—The Higgins Machine.

ment. The impeller-shaft is a continuation of the motor-shaft. The bottoms of the spitzkastens are covered with a slanting air-mat, similar in construction to that in Callow cells. A pneumatic froth is produced, which flows over the discharge-lip of each " spitz " without the necessity of a skimmer. The tailing drops into a box-like arrangement at the foot of the air-mat and

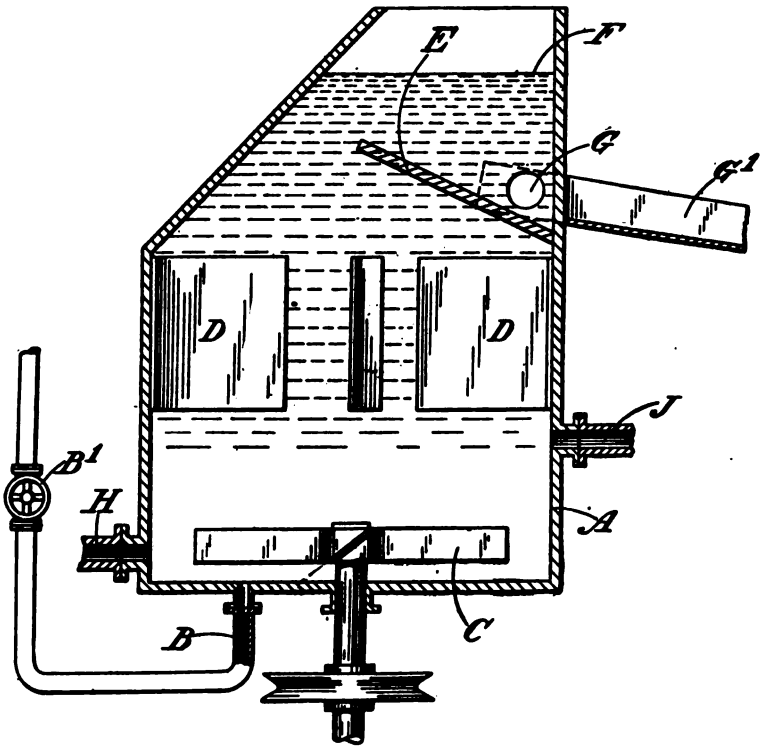


FIG. 12.—Wood Sub-Aeration Machine.

thence passes up over a weir of adjustable height (not shown). The adjustment of the height of this weir regulates the depth of pulp in the spitz. Usually, the weirs require little manipulation after once being set to give proper depth of froth.

The motor uses less power than that of the mechanical machine, averaging 7 hp. per cell. About 150 cu. ft. of air per minute at four to five pounds pressure per square inch is needed for

each machine. Two operators can easily serve a unit of 3000 tons and have to adjust only the amount of air in the wind-boxes and occasionally the oil-feed.

These machines are placed either side by side or end to end, according to the preference of the designer. About five of them

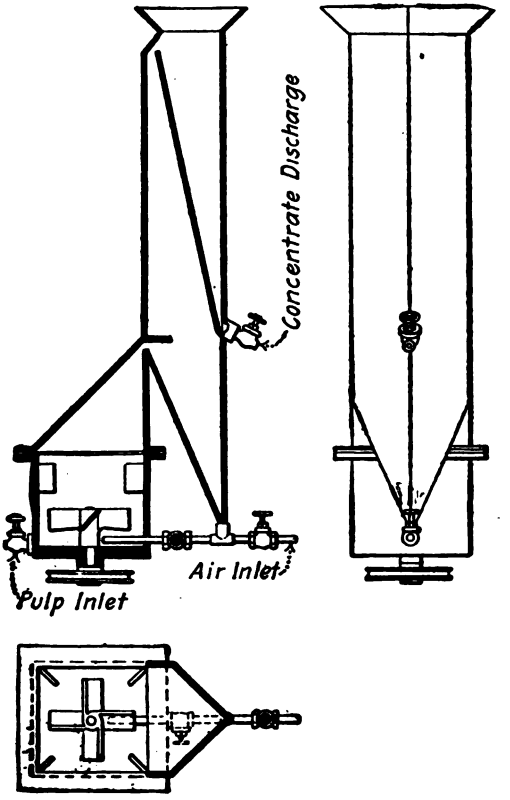


FIG. 13.—Another Design of Wood Machine.

in series are used for roughing and two for cleaning. Such an equipment, together with an emulsifier, treats 150 to 200 tons per 24 hours. By decreasing the amount of air it is possible to raise the grade of the concentrate, but the tonnage is lowered.

The main wearing-parts are the impellers and the liners. A liner will last from three to five months and the impellers two to

three months. A single cell can be shut-down for repairs without disturbing the operation of the others since there is a drop of three feet between them. The motor is lifted off with a small crane, exposing the inside of the agitator-chamber. Replacing a liner or screwing on a new shaft with new impellers occupies only about 20 minutes. Hence practically continuous operation is possible.

Since each cell has an agitating-compartment oil may be added at any step in the series.

The use of individual motor-drive for flotation-cells is parallel with the tendency to do the same with grinding and concentrating machinery. The designers claim that the first cost is not excessive when compared with the cost of belting, shafting, and superstructure necessary for a group-drive. When shafting is used in a group-drive the settling of buildings and other causes bring about friction in the bearings that support the shafting. Stopping to true-up requires a shut-down of the mill, and this is generally not done. The individual-motor drive eliminates all such difficulties and removes a great deal of super-structure, so that a small crane can have proper access to the cells.

The great disadvantage of the Janney machine is its excessive use of power. Where power is cheap the cost is low but in other localities this item is very important. I also question the advisability of using agitators after dissemination of the oil in the pulp has been accomplished. The porous blanket-cells will then froth out all the mineral without the necessity of using more power for agitation. I am indebted to E. Shores of the Stimpson Equipment Co., which makes these machines, for much of my information and for the drawings.

Sub-Aeration Machines.—The mention of the use of air-baskets in spitzkastens of the Janney machine suggests the many devices that call for the use of moving blades in the pulp and the introduction of air. After all, the thing desired is to so attach air or gas-bubbles to valuable mineral particles that they will be floated in a froth. Whether atmospheric air be beaten into the pulp by mechanical swirling or whether compressed air be introduced into the pulp close to the swirling blades, the result is

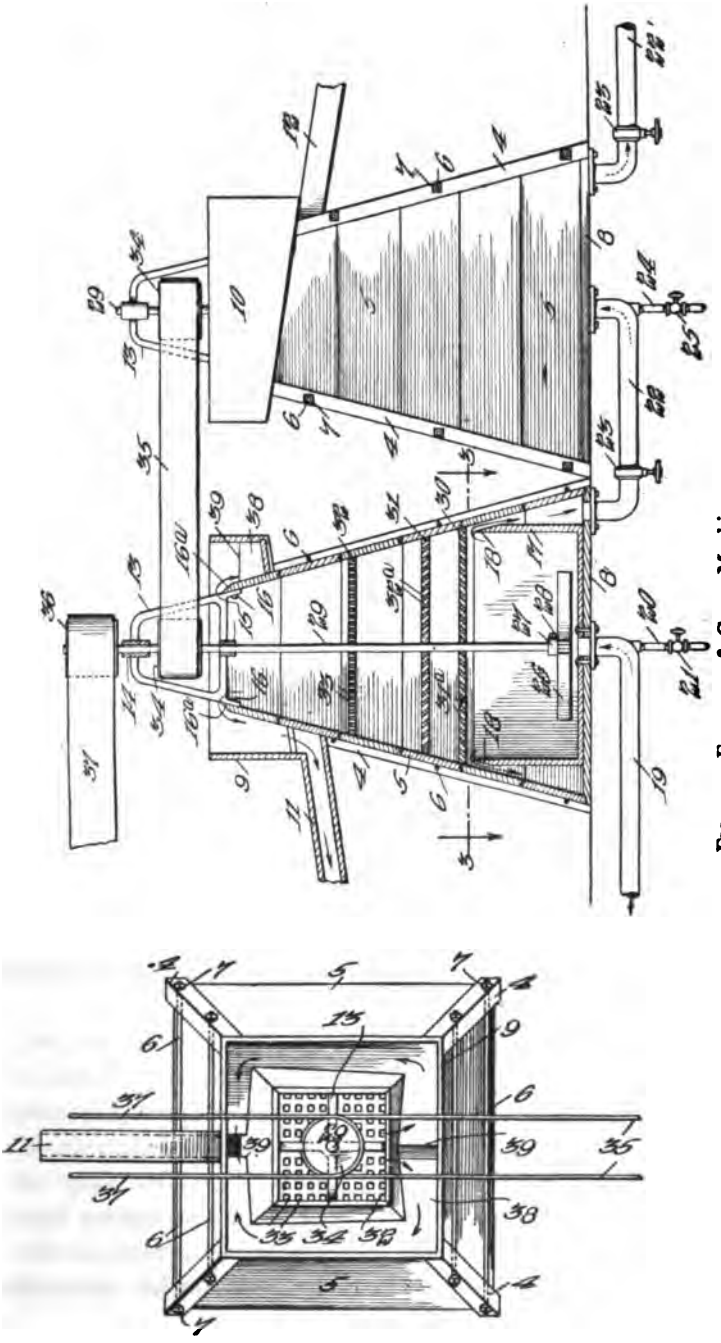


FIG. 14.—Fagergren & Green Machine.

that bubbles of air are caught in the pulp in front of the impellers and are disseminated through the pulp.

A. H. Higgins and W. W. Stenning invented one of the first sub-aeration machines used in the United States by the Minerals Separation, Ltd. It was protected by U. S. 1,155,815 of October 5, 1915, from which is taken Fig. 9. The reason for the designing of such a machine is given in the words of the patentees:

" One object of this invention is to provide an apparatus in which agitation, aeration froth formation, and froth separation are effected in one box or series of boxes without requiring the use of spitzkasten. A further object is to remove the froths immediately they are formed so that a mineral-bearing froth ready for flotation shall not be subjected to further agitation with the pulp. An incidental object is to effect the efficient recovery of so-called ' tender ' froths from which the mineral has a tendency to shower."

These objects are attained by introducing air beneath the impellers through the pipes *E*. The impellers beat the stream of air-bubbles into a fine froth, which immediately rises and strikes the inclined baffle, *J*, which directs it to the left into the box *K*. The pulp issues into the upper half of this box from the box *K* through the openings *L* and the froth rises to the surface, while the pulp in this relatively quiet zone sinks to the top of the baffle *J* and is deflected to the right, passing through opening *F* into the bottom of the next compartment. The drawing shows the compartment farthest to the left as a mixing-compartment without any froth-overflow. Two different shapes of impeller-blades are also shown. The first of these machines was made with the air-pipes *E* open to the air, with the expectation that the violent rotation of the impellers would create suction enough to pull air into these pipes. This expectation was never justified and compressed air was found necessary. Further, the glands where the impeller-shaft passed through the inclined baffles wore out fast and admitted too much air. The impeller-blades and liners of the beating-boxes wear out soon and are inaccessible, and the machine must be taken apart in order to replace them. On that account this particular type of sub-aeration cell is not now being

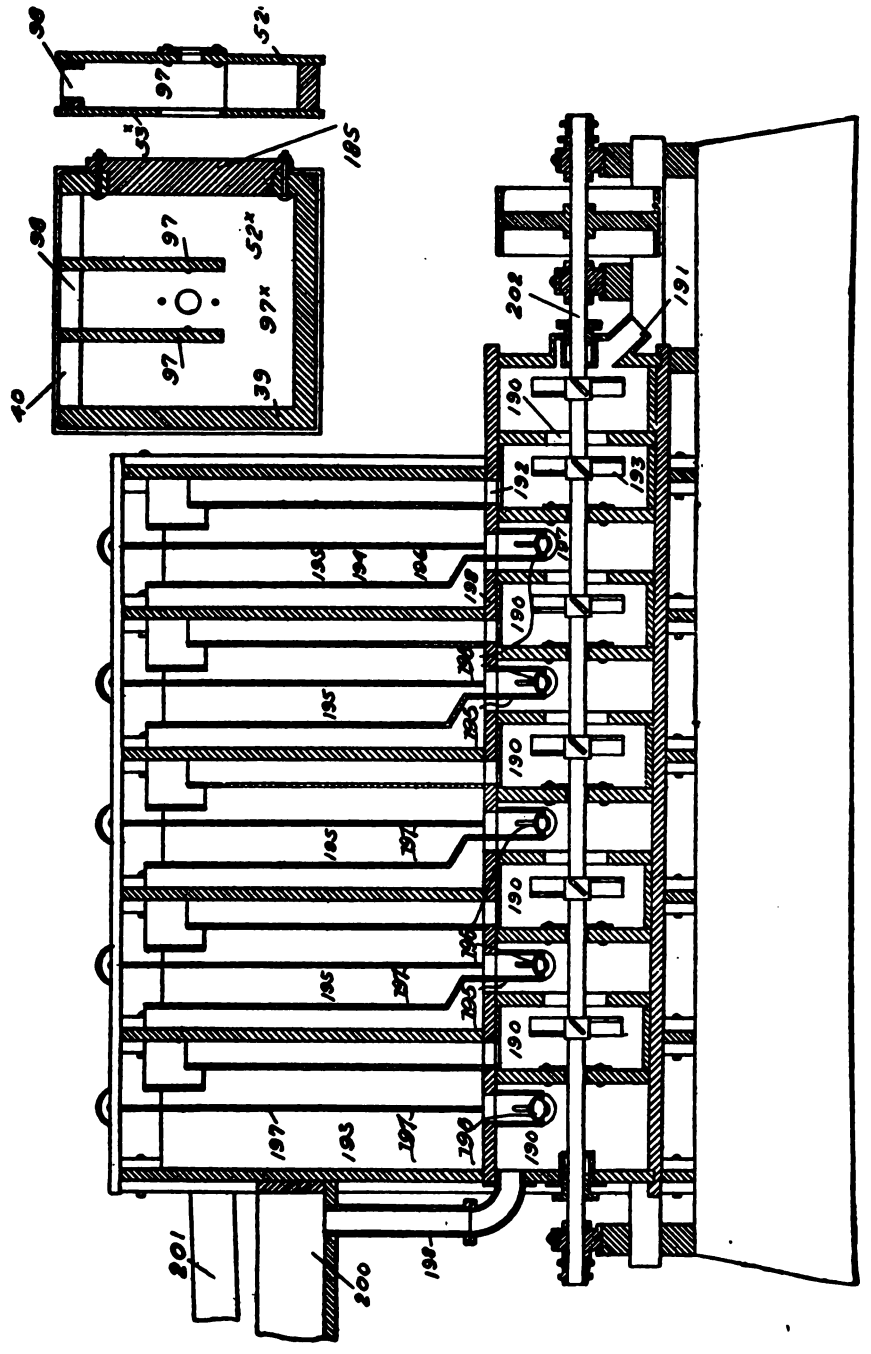


FIG. 15.—The Mishler Machine.

used, although a machine of this pattern was employed for a while at Anaconda.

T. M. Owen has invented a much more practical machine which is protected by U. S. 1,155,836 of October 5, 1915. Air is admitted beneath the impeller through the valve *O* and the pulp is fed into the machine through the pipe *M*. The froth rises as soon as it is formed, as can be seen in Fig. 10. The zone below the baffles *E'* is violently agitated, but the baffles prevent the disturbance reaching the upper portion of the cell and the froth has a

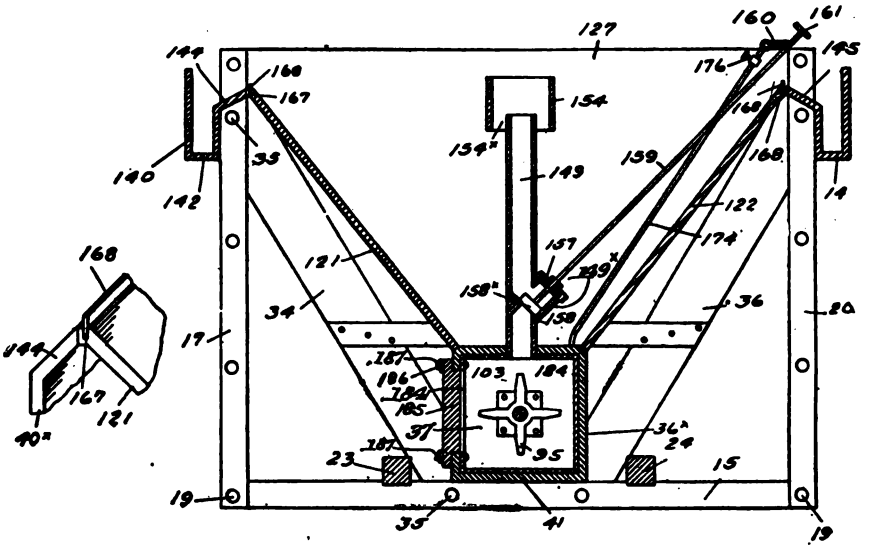


FIG. 16.—Section of Mishler Machine.

chance to separate quietly from the pulp. It overflows into the launder *Q* and the tailing passes out of pipe *T*. This machine is accessible for repairs, as can be seen by looking at the section taken through the line 3–3. Moreover, the construction is simple, being especially adapted to steel-work. The constricted top is characteristic of machinery often used in differential flotation, in which a minimum amount of oil is added in order to cause flotation of only one mineral, and excessive aeration is necessary to build up any depth of froth whatever, on account of its tendency to break.

A. H. Higgins gives alternative designs of many similar sub-aeration machines in U. S. patent 1,155,816 of October 5, 1915. These are shown in Fig. 11. In each case the air-inlet is lettered *E*, the pulp-inlet *D*, and the tailing-discharge *J*.

The patentee claims the following advantages for this kind of machine: It is possible to regulate the amount of gas employed for gaseous selection and flotation. It is also possible to regulate the degree of division of the air by the form and speed of the agitator. These are of great importance, as Higgins claims that different ores and different characters of suspended particles are considerably affected by the total amount of air or its degree of division. Further, the amount of frothing-agent to be used with this apparatus may be considerably reduced from that necessary in the usual apparatus for the agitation-froth process. It is characteristic of this apparatus that it has a continuous admission of air at the bottom and continuous feed and overflow above, so that the upper part of the pulp is in a state of comparative quiet although reinforced constantly by a stream of rising bubbles, so that it overflows continuously.

The Hebbard sub-aeration machine is an even simpler type of construction. A long series of compartments like the standard mechanical type of M. S. machine is used, except that large openings are cut in the walls between the adjacent agitation compartments and the spitzkastens have been omitted. A deep heavy grid is placed in each agitation compartment above the impellers and air is introduced under each impeller. The froth overflows from each compartment into a launder. This machine is in fairly common use on account of its simple construction.

The Hebbard-Harvey sub-aeration machine is an improvement on the Hebbard machine made by R. J. Harvey of the Central mine at Broken Hill. The impellers are driven by shafts passing up through the bottom of the machine instead of coming down from above. This removes the unsightly structure above the machine and allows free access to the top but necessitates the maintenance of a packed gland for each impeller-shaft.

The L. A. Wood sub-aeration machine is a somewhat differ-

ent design, said to be adapted to floating sulphides and other minerals by use of air and without the addition of a frothing-agent or an oil. This is shown in Fig. 12, which is taken from the patent specification, U. S. 1,155,861 of October 5, 1915. The air-bubbles with their associated mineral break; hence a baffle *E* is necessary to catch them. The pulp-inlet is at *H* and the outlet at *J*. Fig. 13 is another design, covered by British patent 10,312, of 1914, also granted to Wood. The process is described as being applicable to the flotation of sulphide ores of copper in neutral pulp at ordinary temperatures; but it has been applied to Broken Hill tailing with the addition of 1% sulphuric acid, and heating to 60° C. is recommended. Differential flotation is also claimed by varying the aeration according to the nature of the ore and the degree of crushing. These patents are assigned to Minerals Separation.

W. Fagergren and W. D. Green, under U. S. 1,195,453 of August 22, 1916, have shown still another design of sub-aeration machine. Its chief claim is simplicity of construction, being made of plain lumber, as can be seen in Fig. 14.

R. T. Mishler, metallurgist for the El Tigre mine, in Sonora, Mexico, has patented a machine in which the agitation-shaft is horizontal and submerged. Fig. 15 and 16 give a general idea of the construction. The pulp-inlet is at 191 and the air-inlet is through pipe 160 and valve 176. The construction seems to be involved and inaccessible although the bolted plate 185, shown in the cross-section, can be taken off for inspection and replacement of the agitators or agitator-chamber lining. The patentee states that the objects of the invention are, " First: To separate the concentrate from the gangue during a repeated agitation of the pulp, in the presence of air or other gas, such agitation being followed by a period of quiescence or separation, when the concentrate rises to the surface, and overflowing, while the gangue settles to the bottom and is subjected to agitation and separation during successive alternating periods, in order to remove the remaining traces of the concentrate. Second: In an apparatus of the character described, to provide a series of alternating agitation and separation chambers. Third: To maintain a

minimum power consumption, by simultaneous agitation of the gangue in the agitation chambers. Fourth: To obtain maximum extraction and grade of concentrate by agitation of the gangue, in the presence of air or other gas, and under the pressure of a considerable height of pulp, thereby obtaining the advantage of the expansion of the gas-bubbles, as they rise to the surface, carrying the concentrate. Fifth: To obtain from the impulses imparted to the pulp by the agitation in all of the separation chambers, an approximately uniform overflow level for the concentrate. Sixth: To prevent resettling of the concentrate, by minimizing agitation in the separation chambers. Seventh: To prevent the settlement of sand, and the consequent clogging of the apparatus; and Eighth: To transfer the pulp from one chamber to another within zones of intense pulp agitation."

Mishler's machine is covered by U. S. 1,197,843 of September 12, 1916. He claims that the novel principle of his invention consists in the agitation of the pulp, while submerged, with introduction of gas at a considerable distance below the surface and under a considerable pressure of pulp. This means a greater volume of air per unit-volume of pulp than is possible when air is merely being churned into the pulp at the surface. He also claims that a cleaner concentrate is produced by the rupture at the surface of a portion of the sulphide-bearing bubbles, the concentrate thus liberated attaching itself to the underlying bubbles, while the liberated gangue slides from their surfaces.

The introduction of air into the suction of a centrifugal pump through which the pulp is passing constitutes another method of sub-aeration. One way of carrying this into effect in a continuous plant is shown in the patent of T. M. Owen (U. S. 1,157,176 of October 19, 1915). The pulp is mixed with the oil and other addition-agents in tank *F* (See Fig. 17) and the air enters the pulp-stream through the pipe *L*. The pump discharges into a frothing-box and the tailing passes out at *O* into the suction of the next pump. Any number of flotation-cells of this construction can be used in series. A crowding cone *C* can be used when the froth is brittle or thin. In this way a close

control of the aeration is possible. Owen recommends this apparatus for differential flotation.

The centrifugal pump is also used in the Bunker Hill & Sullivan mill in a machine similar to that of Owen, but this machine, the invention of R. S. Handy, is of more simple construction. The froth-boxes are built into one long box with partitions in which spaces are left for the gravitation of the pulp from one compartment into another. A centrifugal pump, into whose suction a compressed-air pipe is led, draws the pulp from the bot-

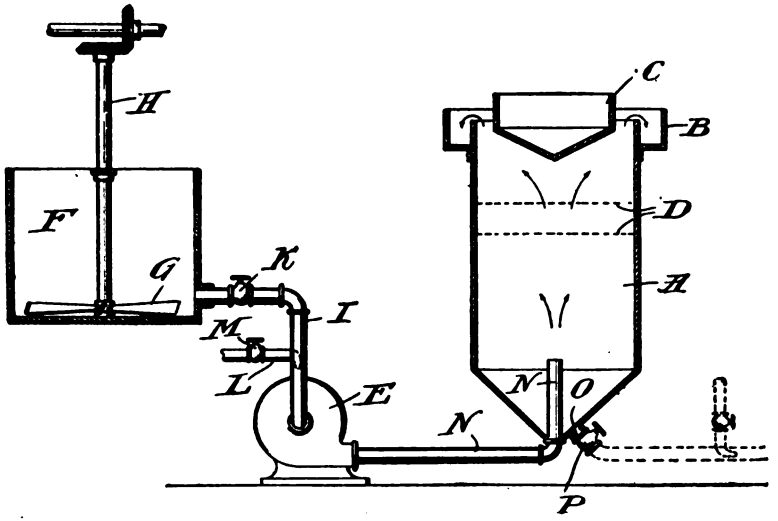


FIG. 17.—Section of Owen Machine.

tom of each pair of froth-boxes and returns it about half-way up the side. The froth rises and is removed by an endless belt with attached rakes. Where pneumatic machines gave a concentrate of 40% lead this machine gives a concentrate of nearly 60% lead, the restricted agitation causing a clean froth to form. Turning the air-valve slightly in either direction is often enough to spoil the froth.

Sub-aeration machines are now much more popular than the older standard mechanical machines, because the use of them decreases the consumption of power and also of oil. Higher recoveries likewise are obtained. Undoubtedly the introduction

of compressed air in flotation-cells usually benefits the operation. Only with an ore or a frothing-agent that gives too much froth is sub-aeration a disadvantage.

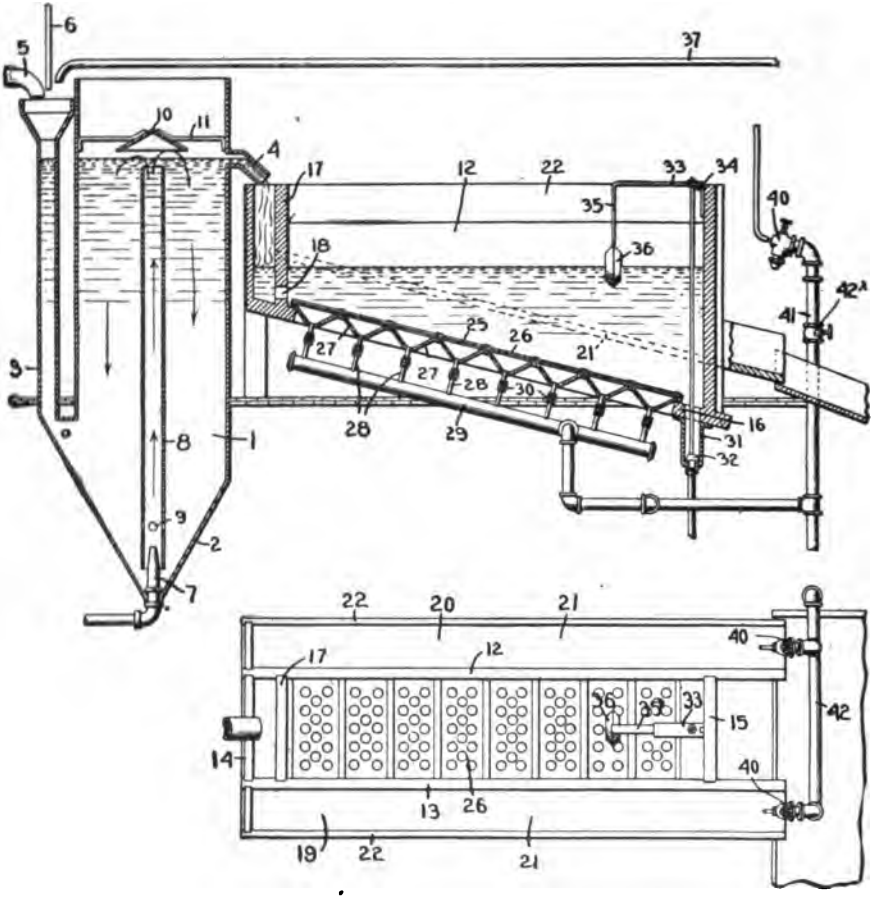


FIG. 18.—Callow Pneumatic Machine.

Pneumatic Flotation Machines.—The use of air for flotation, without mechanical methods for breaking up the bubbles, has undergone notable development during the last two years. At first, the machines were provided with porous media for introducing the air into the pulp, but later this was not always found necessary. On that account pneumatic machines may be divided

into two classes, one in which a porous medium is used and the other in which the air is introduced through jets or under pressure.

The standard Callow machine is the invention of J. M. Callow, one of the pioneers in pneumatic flotation. One fairly common design of this machine is shown in Fig. 19 together with the Pachuca in which the oil is mixed into the pulp previous to flotation. The eight air-distributing boxes at the bottom are usually cast in one block and the bottom is unbolted and removed when the canvas needs replacement. Punched-iron plates are shown supporting the canvas rigidly. Sometimes the canvas is overlaid by wire-screen instead of the punched-iron plates to prevent its bulging out or breaking under the air-pressure, or the canvas is stretched tightly and is not otherwise supported. The construction of the bottom also varies in the manner of holding the canvas in place. In the drawing it is clamped between punched-iron plates. It may be clamped with a special frame that goes over each wind-box; or a groove is cut into the frame all the way around each wind-box and the canvas is driven into this groove and held tightly by pounding in a solid rope slightly greater in diameter than the groove. For removal the rope is merely pulled out and a new canvas can then be placed and roped in.

The round type of Callow cell, Fig. 19, was one of the earlier forms tested by him and was protected by U. S. 1,141,377 of June 1, 1915. A carborundum stone was used as the porous bottom; it was satisfactory except that the continued use tended to cause the pores to choke with dirt and grit. "Filtros" blocks suffered the same fate. Canvas was found best for this work and was later used in all the standard machines. Hence there was no more necessity for building the machine round, to accommodate the use of a carborundum wheel.

The canvas is usually discarded after about six months, for by that time it has become clogged with ore-particles, by grease from the blower, or by dust from the air. In the Chino and Utah Copper mills the air is filtered through cloth by encasing the blower in a room with walls of muslin. Trouble is caused if the

air is turned off while a pneumatic machine is full of pulp and the machine is allowed to stand for a number of hours. In this case the fine slime has an opportunity to settle upon the canvas and cake in its pores. Canvas, being pliable, clears itself of such

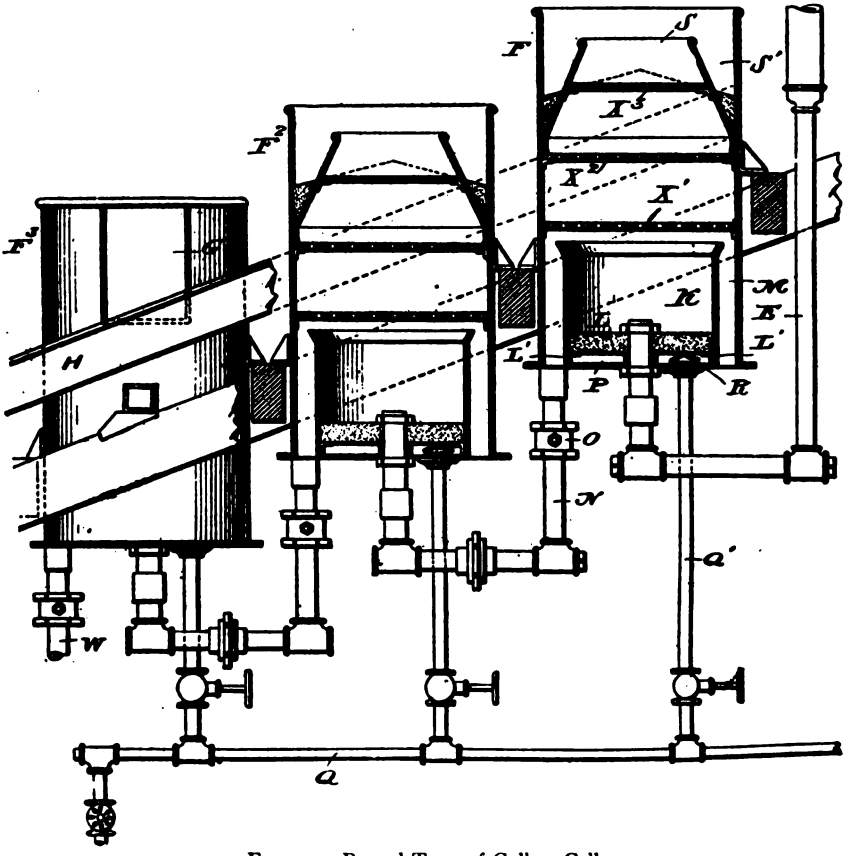


FIG. 19.—Round Type of Callow Cell.

obstruction much more easily than rigid carborundum or "filtros" blocks.

The Callow flat-bottom cell, U. S. 1,182,748 of May 9, 1916, is shown in Fig. 20. The sand is advanced over the bottom by the use of a drag-belt. It is not certain that this is necessary, for the Inspiration machine, described elsewhere, has a flat bot-

tom and the sand slides gradually across the canvas. I have seen such a flat-bottomed cell in use without a drag-belt.

The triple-length Callow cell has more recently been devised for treatment of the finely divided slime of the Cobalt district. It is 29 ft. long and is made from castings intended for three of the standard-length cells. Only pulps containing small percentages of sand can be used, as the slope of the machine is much reduced.

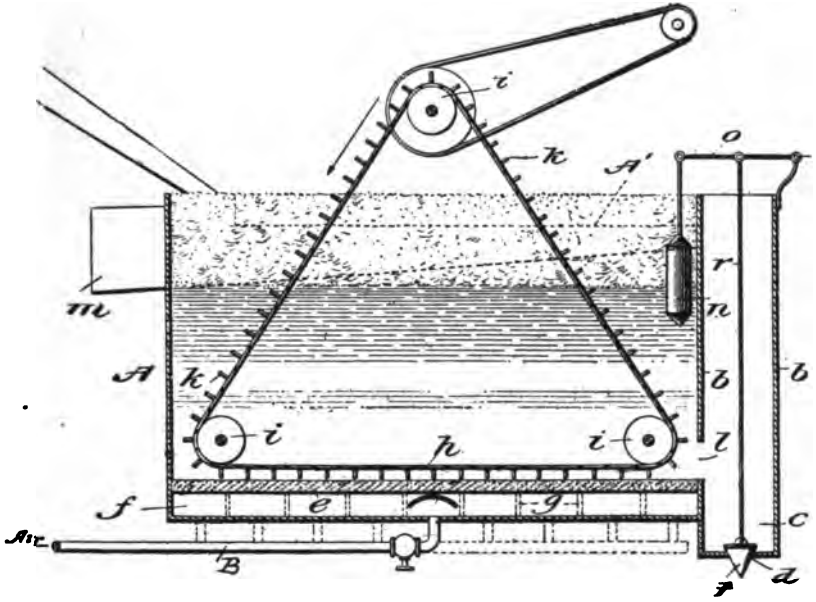


FIG. 20.—Callow Flat-Bottom Cell.

James M. Hyde has described a pneumatic flotation machine in the *Mining and Scientific Press* of August 5, 1916. The individual wind-boxes can be removed without disturbing the others so that the machine can be run continuously while any one of them is removed for replacement of the canvas. The essentials of this machine are shown in Fig. 21 and 22. By having the air-inlet valves directly above the froth in the cell there can be no excuse for operators allowing the distribution of air to become uneven.

A similar machine, used in the Inspiration mill, was likewise developed from the fundamental conception of using a launder with a porous bottom. Its evolution is graphically illustrated

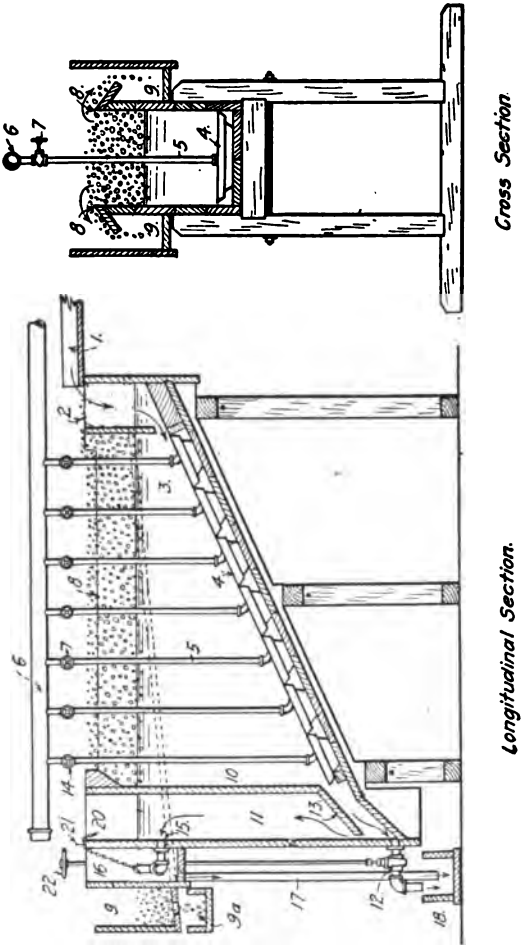


FIG. 21.—Section of the Hyde Flotation Machine.

by Fig. 25, which is taken from the paper by Rudolf Gahl presented at the September meeting of the American Institute of Mining Engineers in 1916. The details of the machine are given in Fig. 26. It consists of a series of boxes with false bottoms of canvas in which frothing is produced by compressed air intro-

FIG. 22.—Showing Method of Dressing Individual Air-Cells.

duced beneath the canvas. The pulp goes from one cell to the next by passing underneath the partition between the two boxes. This arrangement has the advantage of giving a treatment in series, forming a rougher-froth, which is re-treated in a similar set of cells. The sand tends to settle in this machine and at present is stirred occasionally by the introduction of a pipe on the end of a hose, injecting water under 80-lb. pressure. The machine has

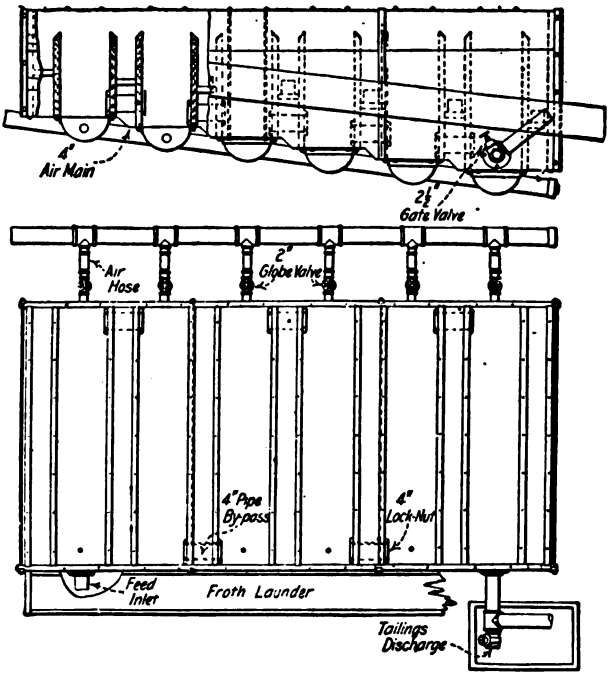


FIG. 23.—Launder or Crerar Machine.

the advantage of great compactness and is easily repaired. The bottom of each cell can be removed without stopping, as the air-line is led down to each individual air-box in a manner similar to the Hyde machine, above described.

It is believed that the principal advantage of the Inspiration machine is the large tonnage that can be treated on a given floor-space. Being almost flat-bottomed the sand tends to collect on

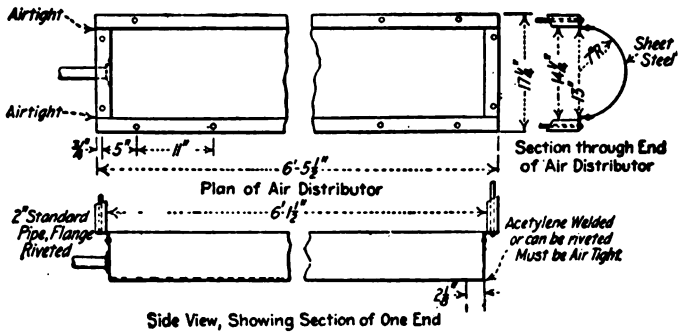

Airtight
Airtight
Sheet Steel
Section through End of Air Distributor
Plan of Air Distributor
2" Standard Pipe, Flange Riveted
Acetylene Welded or can be riveted Must be Air Tight
Side View, Showing Section of One End

FIG. 24.—Sheet-Steel Bottoms of Wind-Boxes.

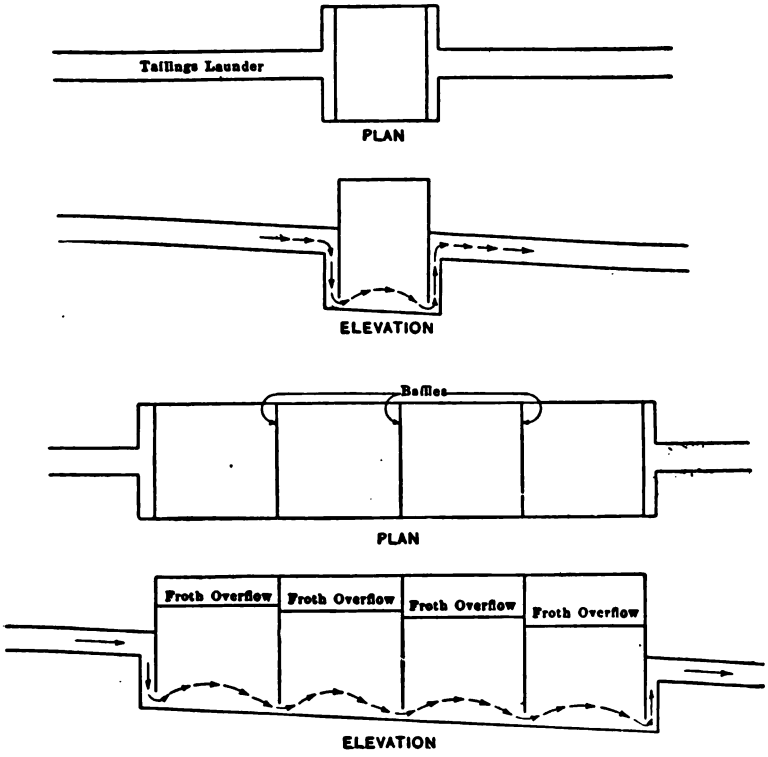


FIG. 25.—Diagram Showing Origin and Development of Inspiration Flotation Machine.

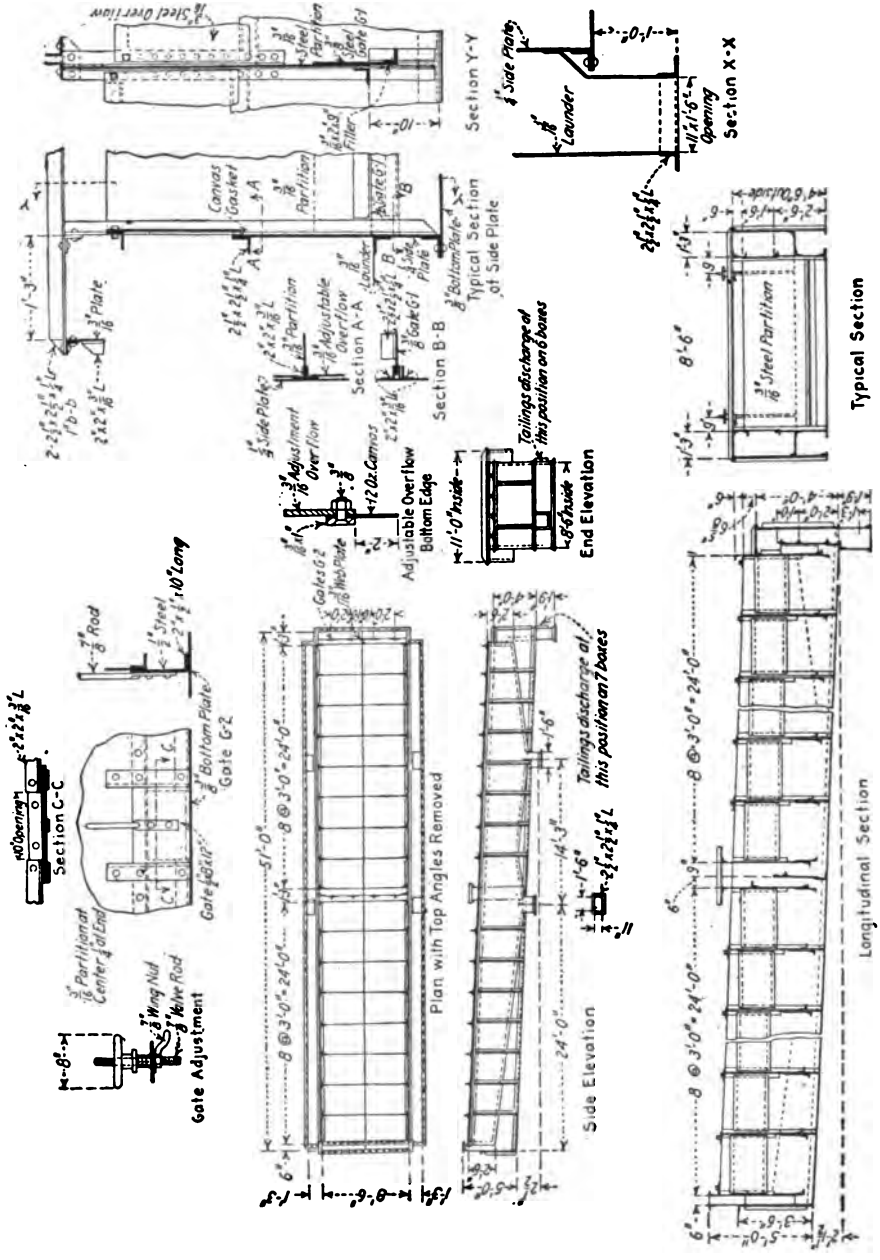


FIG. 26.—Inspiration Flotation Rougher-Cells of Steel Construction.

the canvas and two or three laborers on each shift are kept busy passing a small pipe with high-pressure water jets over the surfaces of the canvas bottoms in each compartment in order to stir the sand and cause it to pass on. For a plant of the size of that at Inspiration the increased cost per ton due to this extra labor is small. The individual air-baskets make possible the removal and replacement of the canvas squares without stopping the machine, one compartment merely running empty and overflowing no froth.

The launder, or Crerar, machine is one in which the pulp passes through a considerable length of launder. It is adapted, as can be inferred, to making a low tailing owing to the length of time that the pulp is in the machine. The speed of advance of the pulp through the machine, however, is faster than in the Callow type in order to obtain the same tonnage. The description of this machine is taken from the *Engineering and Mining Journal*, of December 16, 1916, where it was described by B. M. Snyder. See Fig. 23. It consists of a series of six launders 6 ft. long by 14 in. wide, placed side by side, connected in series with sufficient space between to allow for removal of froth. These are also successively deeper in order to induce a flow of pulp. Fig. 24 shows the construction of the sheet-steel bottoms of the wind-boxes, which are easily made at the workshop of an ordinary mill. The total cost of construction of such a machine is estimated at $458. The air required is 10 cu. ft. per minute per square foot of frothing-area at 3 to 5 lb. per sq. in. This gives an average of about 60 tons daily capacity.

The Fynn-Towne or bubble-column machine was one of those used during the period of competitive testing at Inspiration. It consists of a deep column for pulp with a porous carborundum stone at the bottom for the admittance of atomized air. The machine did not do as well as did the Callow machine during the Inspiration testing so it was discarded by that company.

The C-B frothing-classifier, invented by David Cole and Julius Bergman, of El Paso, is shown in Fig. 27 and 28. Compressed air is introduced into the cell through perforated pipes which are wrapped with canvas to further break up the streams

of air. A series of these pipes is used near the bottom of the cell as seen in Fig. 27, but enough space is left for the sand to drop between the pipes and pass out of the cell. Hence this type of machine is not troubled by the sand in the pulp. The coarse mineral in the sand is table-concentrated after the slime has been floated.

In U. S. patent 1,201,934 of October 17, 1916, Callow gives a modification of his standard cell in which sand is spigoted out at 21 (see Fig. 29) and the slime passes out of a separate pipe,

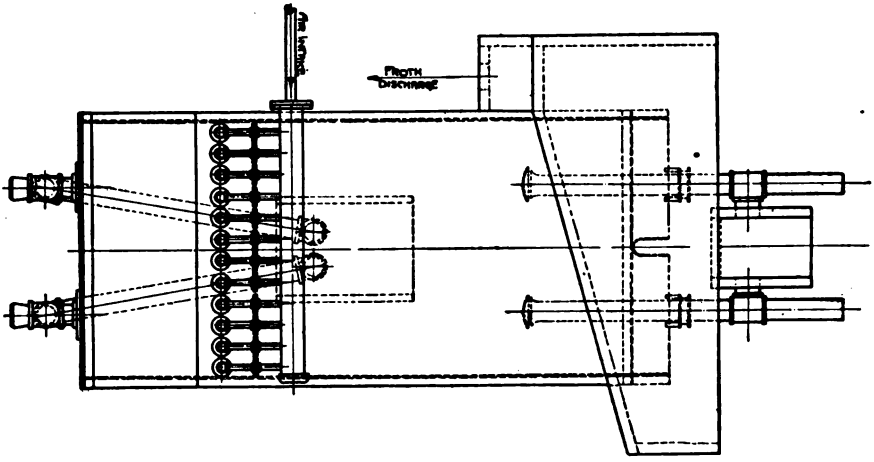


FIG. 27.—Cross-Section of C-B Tube-Grate Flotation-Cell.

marked 24. The sand can then be tabled and the slime treated further by flotation.

It was soon found that the size of the bubbles produced by porous media depended more on the composition of the solution into which they were blown than on the size of the holes in the medium. A rapidly moving jet of air or gas was found to be fairly well emulsified if water containing a frothing-agent was used. A number of machines have been designed to utilize this principle.

Dudley H. Norris invented the " pressure " machine shown in Fig. 30, taken from U. S. 1,167,835 of January 11, 1916. Water is fed into an injector-tube 7 and air is entrained from

tube 8, so that water with an excess of air is allowed to collect under pressure in 4. When this water with an excess of dissolved air is released in the flotation-tank the released pressure allows

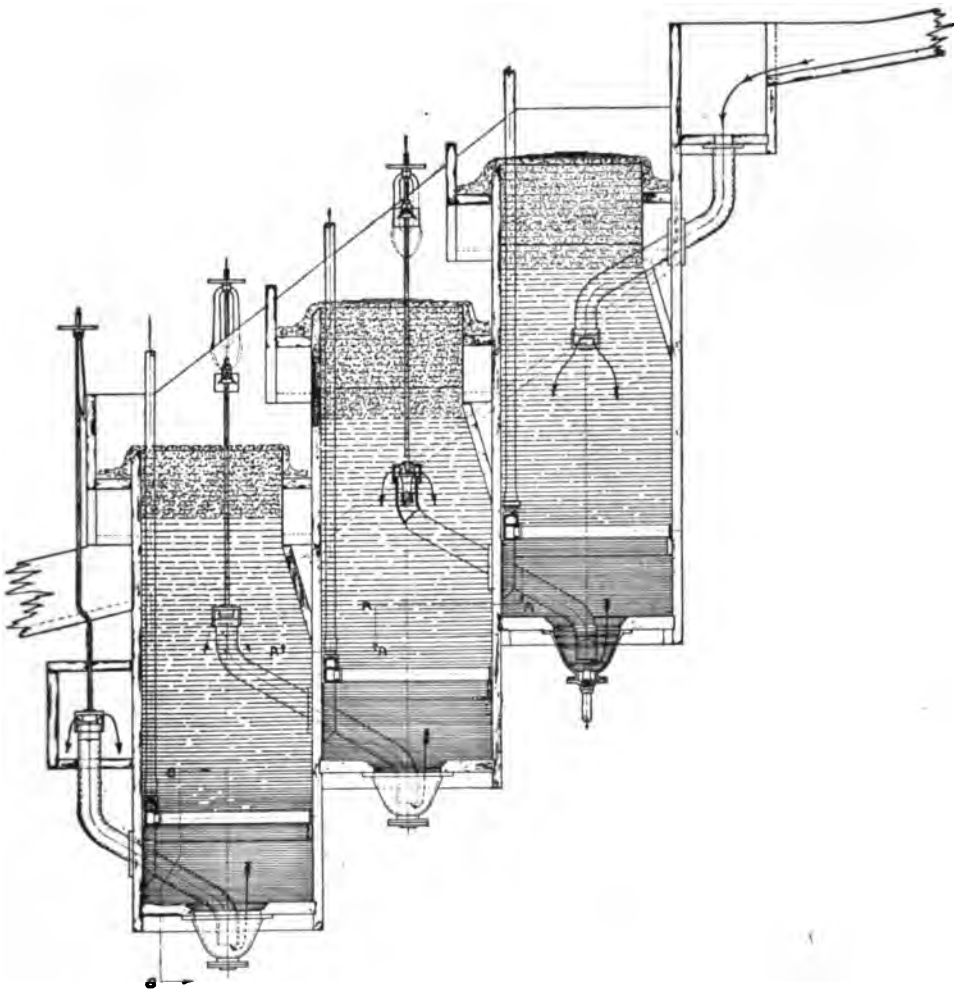


FIG. 28.—Longitudinal Section of C-B Flotation Machine. Three Cells in Series.

the dissolved air to appear in the form of bubbles in a fine state of division. Mr. Norris states that he first had the idea when noticing the water in the wash-room of a Pullman car made milky by dissolved air. As is well known, the water-tank of a Pullman

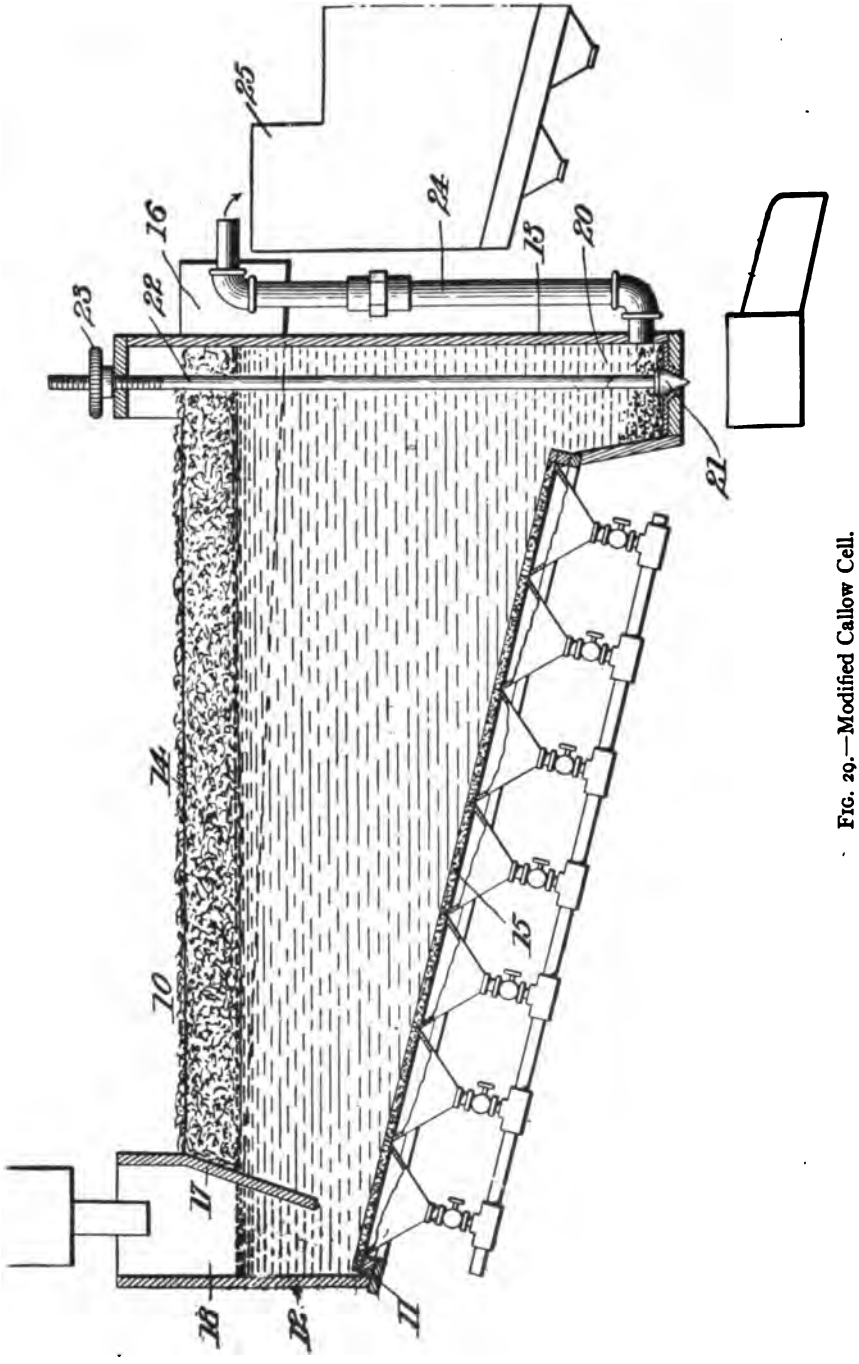


FIG. 29.—Modified Callow Cell.

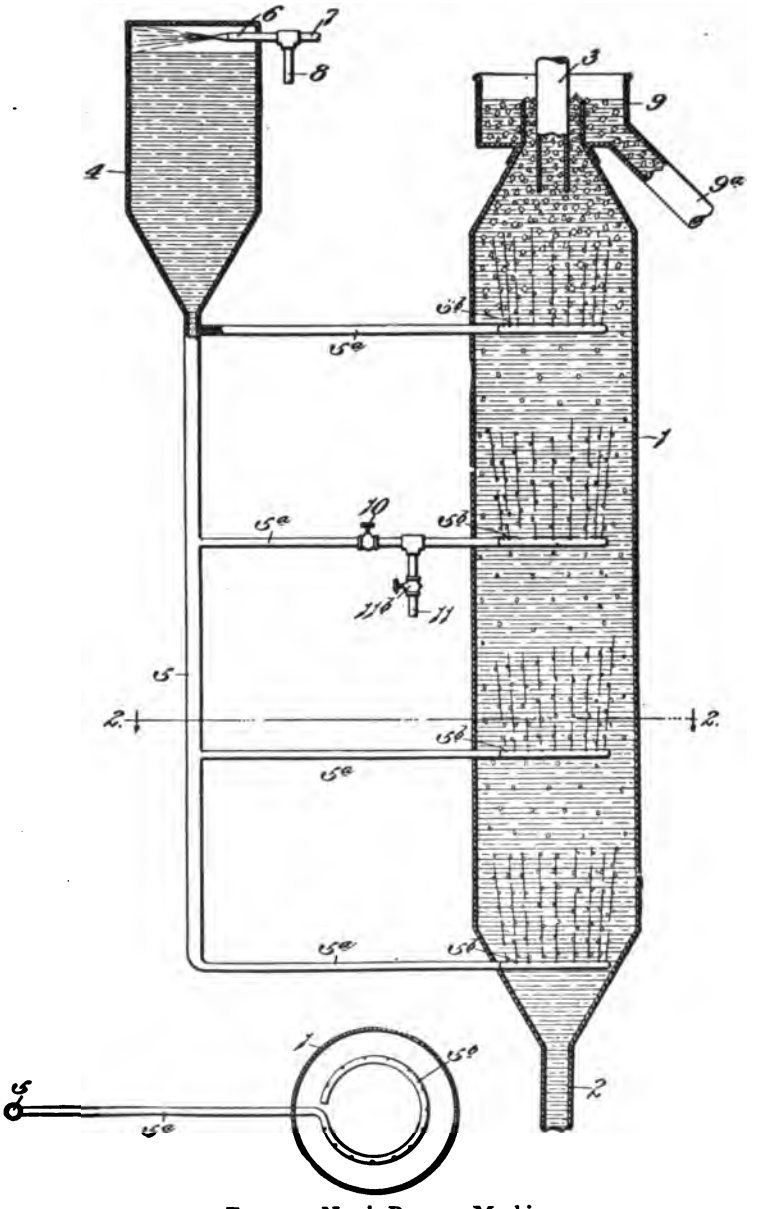


FIG. 30.—Norris Pressure Machine.

car is underneath and air from the brake-system is used to force it into the faucets. As far as I can learn this machine is not now used in any mill, but it is suggestive and very much like some machines now in use.

G. E. Ohrn has invented a machine shown in Fig. 31 taken from his patent U. S. 1,187,772 of June 20, 1916. A jet of steam is fed by the pipe *D* and the oil is allowed to enter through the small inner pipe *E*. The jet plunges into the pulp and air is entrained around the steam-jet. The resulting froth must pass a jet of water *L* arranged to wash out any gangue that tends to stick in the mineral-froth. *J* is the froth-overflow launder and *K* is the

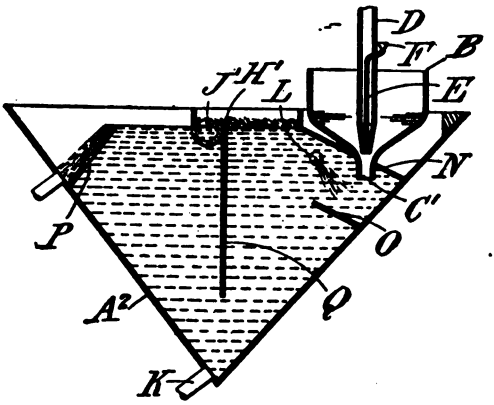


FIG. 31.—The Ohrn Machine.

tailing-discharge. A central baffle can be used to allow slime to overflow separately from the sand. The feed, if desired, can be led into the hopper *B*. The steam tends to vaporize some of the oil and spread it over a greater amount of pulp. This machine was assigned by the Swedish inventor to Minerals Separation as was also his British patent. So far as can be learned the machine is not in use on this side of the Atlantic, but the figures on its operation in Sweden, given out by local promoters, look most interesting. However, steam is a rather expensive medium to use for mixing pulp.

Another steam-jet machine has been patented by Gustaf Gröndal, another Swede, under U. S. 1,202,512 of October 24,

1916. The drawing in Fig. 32 is taken from the patent specification; *a* is a small pipe conveying the frothing-agent; *c* is a steam-pipe; *b* is a Körting steam-jet, which allows the entrainment of a great quantity of air, and *d* is a distributer to allow the air, steam, and oil-vapor to be dissipated through the pulp. The feed-pipe is at *g*. The froth-overflow is at *k* and the tailing-discharge at *m*.

In the case of an ore that requires heating, like some sphale-

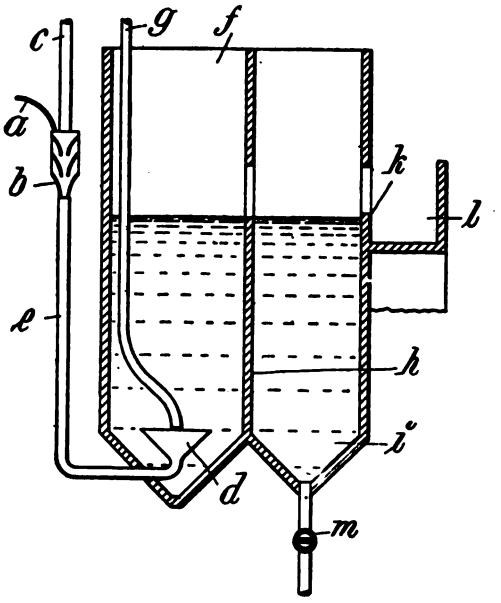


FIG. 32.—Gröndal Steam-Jet Machine.

rite ores, this machine might be useful, because the steam used for heating could also be made to produce the aeration. This patent is assigned to Beer, Sondheimer & Co., formerly agents for Minerals Separation.

J. D. Fields and G. H. Wyman have invented two machines of similar construction. They consist of a series of flotation-cells, each of which has a spitzkasten like the M. S. standard machine, but in place of an impeller in an agitation compartment a jet of air is used in an air-lift for aerating and transferring the

pulp. Wyman's machine was invented several years ago and was used in several localities in the North-West. The Fields machine grew out of an "electrolytic" flotation-cell that proved a failure. After Fields abandoned the use of electricity in his pulp and came down to the use of air for flotation he obtained better results. The Keystone Consolidated Mining Co., in Arizona, has used one of these machines. The box, which is divided into small individual cells, is 30 ft. long, 3 ft. wide, and 8 ft. deep. This is divided into 15 cells, each 2 ft. wide, and an air-hose leads down into the bottom of each air-lift. This machine constitutes the "rougher" unit; a "cleaner" unit of similar construction, but smaller size, is also used. Nothing is known as to the consumption of power, but it is probable that many of the larger air-bubbles escape without doing any useful work. If this be true, this type of machine could not operate as efficiently as a cell using a porous diaphragm.

Film-Flotation Machines.—During recent years not many surface-tension machines have been developed. The Wood machine and the Macquisten tube are well known and need not be described. The engineers of the New Jersey Zinc Co.—G. C. Stone, A. R. Livingston, and L. G. Rowand in particular—have invented various machines of this type.

Stone's machine is not shown here because it does not seem adapted to large-scale work. It consists of a scoop or series of scoops fed with dry crushed ore in a thin layer. The movements of the scoop cuts off the ore-supply and it is lowered at a slight angle into acidified water in a trough. The sulphides float and the gangue sinks. The scoop reverses its motion and passes back beneath the ore-hopper, opening the ore-gate at the bottom by properly arranged catches. The reversal of the motion of the scoop closes the ore-gate and the scoop tilts and descends into the water again. The machine therefore is intermittent in action and of complicated design. It is covered by U. S. 1,156,041 of October 5, 1915.

Livingston's machine is covered by U. S. patent 1,147,633 of July 20, 1915. Fig. 33 shows that it is a much enlarged Macquisten tube, being six feet in diameter and about ten feet long.

The ore is fed through launder *D*. The rotation of the drum carries the pulp up to the left and tacks or brads are used to en-

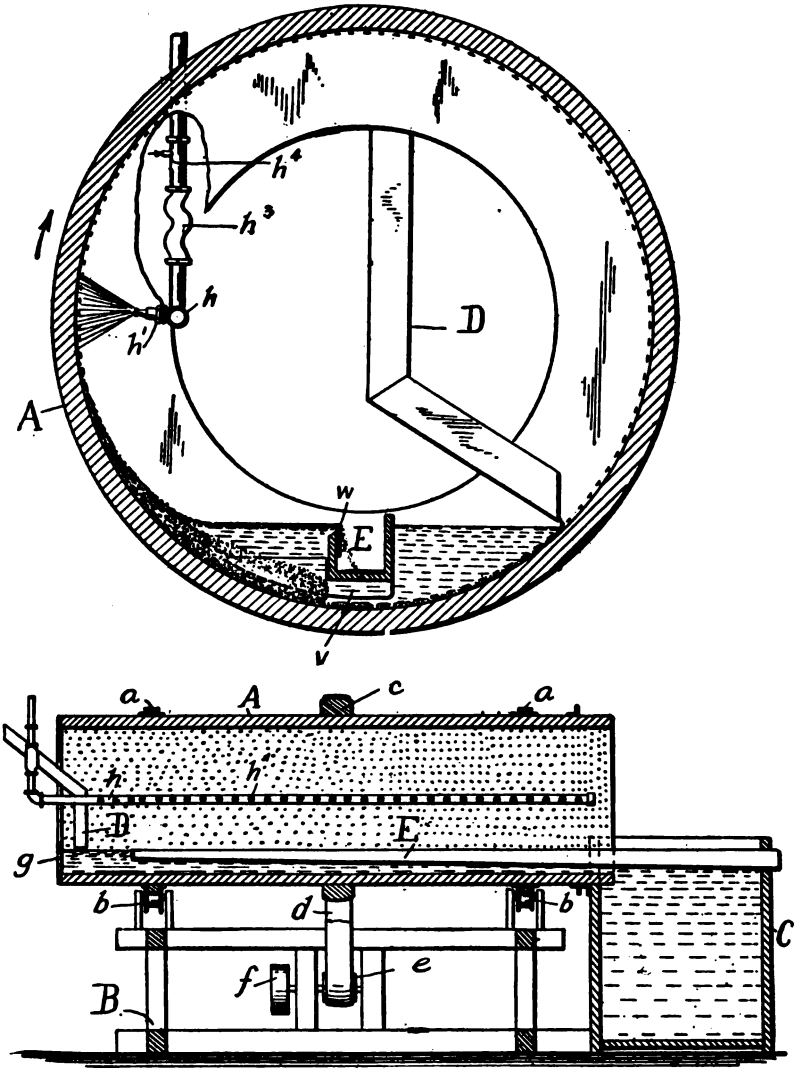


FIG. 33.—The Livingston Machine.

train more ore so that it will be lifted out of the water into the drum. A row of water-jets sprays the wall of the tube above

the rising layer of ore, washing it down and floating the sulphides as a skin concentrate that overflows the side of *E*, a launder, which discharges the concentrate outside the machine while the tailing advances by motion of the drum until it falls into the box *C*. The advancing of the pulp from the back end of the drum to the front is accomplished by slanting plows placed on the underside of the concentrate-discharge launder. The machine was said not to have been successful until the tacks were introduced or retaining the main body of ore while the surface was being washed by the descending jets of water. The descending particles of ore enter the water at so slight an angle and so quietly that the sulphides are easily floated. Aeration of the incoming water is recommended and this is accomplished by the use of the aspirator h^3, which sucks the air in at h^4. Relatively coarse material, 16 to 20-mesh, is said to be best adapted for treatment in this machine and the patent specifications state that some cheap oil and acid improve the operation. Data for tonnage, power, acid, oil, and labor are not available but it can be seen that it is a considerable improvement over the Macquisten tube, being a machine of much larger capacity.

Rowand's machine is covered by U. S. 1,159,713 of November 9, 1915. A sketch of the machine, taken from the patent specifications, is given in Fig. 34. *B* is the chute through which powdered ore, not coarser than 16-mesh, is dropped in a thin layer on a moving belt *e* covered with a film of oil. The oil is stored in compartment *D*, into which the belt dips before the ore is fed onto it. The ore meets the water at *f* and the skin of concentrate is discharged over the lip *d* into the launder *c*. Water is fed through the valve *b* and the tailing discharges at *a*. Like Wood's machine, the speed of the belt determines the movement of the laden film on the surface of the water. No data have been issued on the speed of the belt or the tonnage. It is possible that, as in most skin-flotation machines, slime cannot be treated, only fine sand. The oiling of the sulphide particles before entering the water probably is done most neatly by this arrangement.

Such machines are not widely applicable because they do not

separate slime cleanly. They are best adapted to the treatment of table-middlings that consist of minerals of nearly the same specific gravity, such as sphalerite, barite, siderite, fluorite, and pyrite.

General Considerations.—Mechanical, pneumatic, and skin-flotation machines have been considered separately. In many cases it has been found advantageous to use both mechanical and pneumatic machines in series on the same pulp for the reason that one may do good work on the sand while the other does good work on the slime constituent of the pulp. Experience has shown

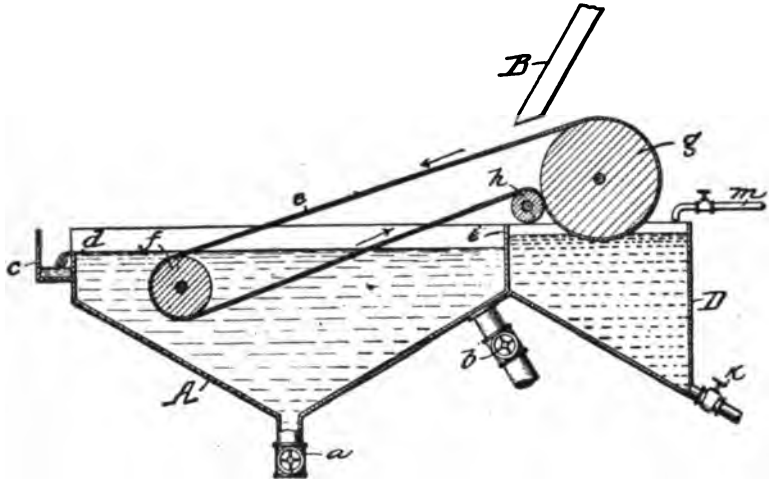


FIG. 34.—The Rowand Machine.

that it is inadvisable to compare mechanical with pneumatic machines but that they supplement each other well. In the order of decreasing coarseness of the pulp that they will treat successfully we have skin, mechanical, and pneumatic machines. There is an apparent exception to this rule if the flotation machine is made to disperse the oil, as a very " colloidal " slime can then be treated best by a mechanical machine that gives intense agitation. If the oil is fed into the tube-mill or other grinding machinery before the pulp reaches the flotation machines, no further dispersion is necessary and a pneumatic machine will show an advantage.

THE FLOTATION OF OXIDIZED ORES

By Glenn L. Allen and Oliver C. Ralston

Introduction.[1]—Concentration of sulphide ores by flotation has met with such success that attempts have recently been made to apply the process to the flotation of ores other than natural sulphides. Most of the experimental work in our laboratory at the Utah station has been done on the oxidized ores of lead. Only minor attention has been given to the oxidized ores of zinc and of copper, for the following reasons: little success has been had with the zinc ores; many others are engaged in testing copper ores, so that there was no pressing necessity for experimentation with copper ores by the Bureau, although an attempt has been made to co-ordinate the work of those who are willing to join in solving the problem. Flotation of oxidized minerals depends upon a preliminary "sulphidizing" by any method that will convert at least the surface of the mineral particles to a sulphide of the metal. This step is followed by flotation of the artificial sulphide.

Patents.—The first method for the flotation of oxidized ores to appear in patent literature was that of F. B. Dick. It is contained in British patent 16,667 of 1908. This method calls for the reduction of the oxide to metal in a furnace with a reducing

[1] This review of the subject is based mainly on a paper, by the same writers, issued by the U. S. Bureau of Mines in July, 1916. There has been added a discussion of the patent literature dealing with the subject. The text also is altered somewhat to include more recent information. Most of the portion concerning flotation of lead-carbonate ores has been revised by Mr. Allen, who has continued his work while in the employ of the Shattuck-Arizona Copper Co., in whose Bisbee mine a large tonnage of lead-carbonate ore has been disclosed while mining copper ore. N. C. Christensen and R. W. Johnson have assisted in collecting some of the evidence on which the conclusions of this paper are based.

atmosphere, followed by the flotation of the " prills " of metal formed. As lead and copper are the only two common metals easily reduced to the metallic form, it is probable that Dick had no others in mind. He mentions the oxidized ores of copper in silicious gangue from the Benguella and Katanga districts of Central Africa as being amenable to this kind of treatment. From the coarse grinding recommended by him (20-mesh) it is probable that he had in mind either the film or the bulk-oil types of flotation.

In British patent No. 8650 of 1910, Sulman & Picard, of Minerals Separation, Ltd., have patented a like idea, evidently with froth-flotation in mind. They claim the application to metals in " easily reducible oxides." Such metals as lead and copper are mentioned. One specific application is the treatment of mixed zinc and lead oxidized ores. The lead can be reduced easily in a reducing atmosphere at 600° C. while the oxidized zinc compounds are unaffected at this temperature. After cooling the reduced product out of contact with the atmosphere the lead could be floated away from the zinc. We have not tested this process thoroughly but we are inclined to believe that oxidized forms of copper are more likely to be reduced to an easily separable form than oxidized forms of lead. However, in the examination of the reduced product of copper prepared by others for proposed gravity-separation small shots of metallic copper could be seen attached to the gangue. After the reduction it would be necessary to grind the product to liberate the " prills " and " leaves " of metal from the gangue.

Treatment of complex sulphides by this process assumes that the ore is first roasted to oxides before reduction. In case part of the metallic sulphides is roasted only to sulphates these would tend to be reduced to sulphides again during the reduction period. In the case of mixed lead and zinc sulphide ores it would be all right to allow the lead to roast to sulphate (which is easily accomplished), but any sulphate or basic sulphate of zinc would be undesirable, because the sulphide of zinc formed would tend to float.

The first American patent covering sulphidizing and flotation

is that of Alfred Schwarz (U. S. 807,501 of December 19, 1905). It was taken out coincidently with other patents covering methods of bulk-oil flotation, for froth-flotation was only then being started. He claims the use of any "soluble sulphide" and states that he generally uses an excess of sulphur over that theoretically necessary to convert the oxide, carbonate, or chloride of the metal in question completely to the sulphide. A poly-sulphide of sodium made by boiling sulphur and caustic soda is mentioned.

The next mention of sulphidizing and flotation of oxidized minerals was in British patent 26,019 of 1909 by Sulman & Picard. This patent shows familiarity with the sulphidizing and flotation of ores. While oxidized copper ores are given a prominent place, the sulphidizing of oxidized ores of lead is also mentioned. Hydrogen sulphide, as well as other soluble sulphides, is said to be suitable, and it is here that the use of sulphur vapor is first mentioned in patent literature. One variation of this method is to heat the powdered ore with pyrite in a neutral or reducing atmosphere. Such treatment distills the feeble atom of sulphur from the pyrite, so that the sulphur combines with the oxidized lead.

Joseph T. Terry, in U. S. 1,094,760 of April 28, 1914, describes the use of hydrogen-sulphide gas in a flowing pulp of an oxidized ore of copper (other metals also are claimed) with a suitable apparatus for the recovery of any excess gas after sulphidizing the pulp. The use of sodium sulphate is also described and the addition of copper sulphate to help in the formation of nuclei of copper sulphide around which the formation of sulphide granules and coagulations can take place.

H. B. Hoveland and G. B. Frankforter entered the sulphidizing field with U. S. patent 1,098,668 of June 2, 1914. This claims the application of hydrogen-sulphide gas to dry ore for the sulphidizing of oxidized minerals previous to flotation. It claims advantage in the greater rapidity of the sulphidizing reactions, 10 to 20 minutes in an atmosphere of hydrogen-sulphide gas being said to be sufficient. From the known great velocity of diffusion of gas molecules as compared with the velocity of the

diffusion of the same molecules when in aqueous solution, such a claim seems justifiable. Our own experience on lead ores does not verify this statement, as will be seen later. However, Hoveland and Frankforter mention the carbonate ores of copper in illustrating their process while our work has been confined largely to the carbonates of lead. A surprising claim is made for the sulphidizing of an oxidized capping in place. The patentees state that the gas molecules finally penetrate to the centres of the masses of ore, sulphidizing the oxidized minerals of copper and disintegrating the rock so that it can be more easily mined.

Raymond F. Bacon, in U. S. 1,140,865, of May 25, 1915, discloses the use of hydrogen sulphide and sulphur di-oxide in a pulp to effect flotation by means of the colloidal sulphur resulting from the reaction of these two chemicals. The colloidal sulphur is said to serve as a substitute for flotation-oil. By introducing hydrogen sulphide first the oxidized minerals can receive a sulphide coating before the excess of hydrogen sulphide is neutralized by the introduction of sulphur di-oxide. This feature is embodied in another of Bacon's patents, No. 1,140,866 of May 25, 1915, and is described in connection with some tests of an oxidized copper ore. "One ton of oxidized copper ore containing 2% of copper, and crushed to pass a 60-mesh screen, is placed in a Pachuca tank with three tons of water. The air is turned on and the water agitated for a few minutes, just enough to obtain a good mixture of the ore and water. Immediately after the violent agitation has ceased and while considerable of the ore is still in suspension hydrogen sulphide is forced into the body of ore and water through suitable inlet-pipes in the bottom of the Pachuca tank. With the ore used in this experiment 60 cu. ft. of hydrogen sulphide was admitted. This amount of hydrogen sulphide is not sufficient to convert all the oxidized copper present into the sulphide, but for purposes of flotation this is not necessary. It is only necessary to form a surface-film of copper sulphide surrounding each oxidized particle. The mixture of ore and water is allowed to stand a few minutes with the hydrogen sulphide, then a slight excess of sulphide di-oxide is run in through the inlet in the bottom of the tank. The sulphur di-

oxide gas used for this purpose may be the pure gas or dilute impure gases such as smelter fumes. In case the latter are used they may be introduced in place of air to effect the agitation of the mixture. A short time after the introduction of the sulphur di-oxide the mixture of ore, water, etc., is tested with lead-acetate paper and when the hydrogen sulphide has disappeared the mixture is allowed to flow into a flotation-tank, where the sulphide-coated copper oxide, carbonate, and silicate particles are floated off and thus separated from the gangue. With the particular ore cited, a recovery of 83% of the copper was thus effected, the concentrate containing 21% copper."

Our own tests show that it is very difficult to obtain flotation after the pulp has been treated with sulphur di-oxide. Sulphur di-oxide and the sulphites are known as inhibitors of flotation, and yet Bacon makes the claim that better flotation is obtained in the presence of a slight acidity due to sulphur di-oxide. Bacon's process is not as simple as it sounds.

In U. S. patent 1,197,589 of September 12, 1916, he has still further broadened his claims, and states that this patent is an improvement over his former method. This patent is well written. He has reversed the order of application of the two gases. Sulphur di-oxide is applied first in order to convert all of the copper to sulphite and the subsequent treatment with hydrogen sulphide precipitates the copper as sulphide. He states that it is not necessary to obtain complete solution of all the copper before precipitation although it may be best with some ores. Colloidal sulphur, from the reaction of sulphur di-oxide on hydrogen sulphide, is also produced and the claim is made that this acts as a substitute for flotation-oil in whole or in part, resulting in better flotation. In case an ore contains lead, copper, and zinc the copper and zinc go into solution. The hydrogen sulphide precipitates only the copper from solution and it is then floated out. A subsequent precipitation of the zinc with an alkaline sulphide renders it amenable to subsequent flotation. We regard this as a most extravagant claim.

A few months later Hoveland took out another patent for the sulphidizing of minerals, U. S. 1,159,942 of November 9,

1915. It is claimed that in the application of calcium sulphide for the sulphidizing of minerals the action is greatly accelerated by the presence in the solution of some ferric sulphate. Sulphuric acid, or sulphur di-oxide and oxygen, is first applied to the ore-slime to form copper sulphate. On addition of calcium poly-sulphide and ferric sulphate to the pulp copper sulphide is formed and can be removed by flotation. The function of ferric sulphate is to oxidize any excess sulphurous acid. We fail to see the advisability of getting copper into solution and then re-precipitating it as sulphide, except that flotation serves as a substitute for filtration. Since lead carbonate does not go into solution, the same advantages are not obtained and this method offers no apparent advantage when applied to lead ores.

Later Hoveland obtained two more patents; these covered the use of apparatus for carrying his invention into effect. These patents were 1,164,188 and 1,164,189 of December 14, 1915. The idea that seems uppermost in his mind is that of sulphating the ore by treatment with sulphur di-oxide and oxygen under pressure in a specially constructed agitating-apparatus, arranged for continuous operation. He claims that the sulphating under pressure of minerals like copper carbonate in such an apparatus is much quicker and more complete than at ordinary atmospheric pressure. Here he explains that in order to sulphidize the sulphated material well with calcium poly-sulphide the excess of sulphur di-oxide can be oxidized by the presence of ferric sulphate. In fact, we believe that Hoveland could not conduct flotation well if sulphur di-oxide or sulphites were present in his pulp in any considerable quantity. His apparatus is also adapted for flotation in a closed vessel, so that the same air could be used over and over again for flotation, and if necessary some other gas than air could be employed, in order to prevent re-oxidation of the precipitated copper sulphide.

Bacon was the next patentee (U. S. patent 1,180,816 of April 25, 1916). His patent covered the use of hydrogen sulphide under pressure during sulphidizing. One of the most recent ideas is contained in his patent No. 1,197,590 of September 12, 1916. This deals with both oxidized ores and those that can be wholly or

off of the sulphide film, so the more gentle treatment possible in a Callow cell was tried. Practically identical results were obtained. It was found that with longer treatment with hydrogen sulphide the extractions increased on both silver and lead. Hence the trouble with the early tests must have been due to insufficient time of gas treatment. It was surprising to see the way in which the gas would react with the ore. When placed in a bottle on a rolling agitator the ore would be showered through the atmosphere of hydrogen sulphide like the material in the old Bruckner furnace. The ore would begin to blacken almost immediately and would absorb the hydrogen sulphide with such

Table I

Sulphidizing with dry hydrogen sulphide.
Ore from May Day mine, Utah. 4.2% lead, 2.36 oz. silver, 4.6% iron, 84% insoluble.
500 gm. per test, Janney machine. Oil 0.9 lb. per ton. (SunnySouth pine-oil No 5)

No.	Sulphidized Minutes	H_2SO_4 added during flotation	Weight Gm.	Froth, Analysis, and Recovery.							
				Lead		Silver		Iron		Insoluble	
				Assay %	Recovery %	Assay oz.	Recovery %	Assay %	Recovery %	Assay %	Recovery %
1	15	none	31.3	13.3	20.1			11.7	15.9	60.0	4.5
2	30	"	22.5	9.6	10.1			17.1	16.7	58.1	3.2
3	60	"	40.5	13.7	26.4	5.74	19.7	10.4	18.3	60.6	5.8
4	120	"	54.0	8.7	22.3	3.28	24.2	16.9	39.7	60.7	7.8
5	480	"	93.0	9.5	42.0	4.24	33.4	14.7	59.5	58.6	13.0
6	15	95.7 lbs. per ton	23.5	22.9	25.6	16.00	31.9	20.1	20.5	30.2	1.7
7	30	"	36.6	21.6	37.5			17.5	27.8	33.2	2.9
8	60	"	38.5	21.3	40.1	13.50	45.2	16.1	27.7	35.0	3.3
9	120	"	52.0	25.3	62.7	11.70	51.6	11.3	25.6	38.6	4.8
10	480	"	68.0	24.6	79.7	9.60	55.3	10.4	30.7	37.4	6.0

avidity that a considerable amount of heat was generated. Even after eight hours treatment with the gas it took only a few minutes for the ore to use up all of the hydrogen sulphide remaining in the bottle so that no smell of hydrogen sulphide remained.

The second group of experiments in Table I shows plainly that the use of acid in the flotation of the sulphidized pulp is absolutely essential both for getting higher recovery of the lead and silver from the sulphidized ore and for giving a suitable grade of concentrate. It was found that this ore used less acid than many of the other ores treated and that most of them called for amounts of acid nearer to 300 lb. per ton of dry ore before a clean concentrate and a higher recovery could be obtained. Such quantities of chemicals are, of course, prohibitive unless they can be obtained very cheaply.

A noticeable concentration of iron appears in the flotation concentrate. The iron present in this ore was largely limonite. It was determined by visual examination that the iron was blackened by the hydrogen sulphide, thus accounting for its presence in the concentrate.

Application of the hydrogen sulphide to the ground ore suspended in water gave similar recoveries and grades of concentrate, the only difference being that the amount of gas used was much smaller and it was occasionally possible to get fair work done in a neutral solution—a great advantage. On the whole, we think it improbable that hydrogen sulphide will be used on dry ore on account of the amount of chemicals required. Large lumps of the ore when exposed to the hydrogen sulphide in a bottle reacted vigorously, and on breaking them open it could be seen that the gas had penetrated deeply. Hence, we feel justified in stating that when sulphidizing the dry ore enough gas must be applied to convert all of the lead in the ore, together with some of the oxidized iron, into sulphides. On flotation, the application of acid will break up the iron sulphide with evolution of hydrogen sulphide (this was observed), while lead sulphide is fairly stable in acidified solutions. As the hydrogen sulphide is liberated in the body of the ore by the action of the acid, it is possible that the gas sulphidizes some of the lead and silver that may have escaped reaction previously. Further, after the iron is dissolved by the acid there is probably more of the lead sulphide exposed to the action of the flotation-oil; hence higher recoveries and better grades of concentrate were obtained in the tests where sulphuric acid was added during flotation.

All of the above shows that the particles are not merely "filmed" but are entirely converted to sulphide of lead. In the wet pulp it was possible to use much less than the theoretical amounts of hydrogen sulphide and to get better recoveries, so that only a "film" on the lead carbonate particles could have been transformed. However, sulphuric acid was still necessary in order to get clean flotation after sulphidizing in the wet pulp. As most of the lead carbonate ores contain considerable amounts of acid-soluble material, the consumption of acid was always

high. This caused us to turn to the alkaline sulphides as a method of sulphidizing.

Much of the old literature has insisted that the presence of hydrogen sulphide in the pulp during flotation is deleterious, so we were much surprised that some of our best work was obtained when a sulphidized pulp was acidified, giving a noticeable odor of hydrogen sulphide. Therefore, we conclude that for the artificial lead sulphides, at least, the former belief does not hold.

Commercial methods of making hydrogen sulphide are available if a demand for the gas should be created; in fact, it is being used on the Magma ore at Superior, Arizona, with marked success. The simplest method of making the gas, and one with which practically every engineer is familiar, is the treatment of iron matte with sulphuric acid. Iron matte can be made at a cost of from $5 to $10 per ton by distilling the feeble atom of sulphur from pyrite and melting the residue. Sulphuric acid is available at from $5 to $20 per ton in many mining districts. This will make the hydrogen sulphide cost from $30 to $60 per ton. Hydrogen sulphide can also be made from calcium sulphide by treatment with carbonic acid gas—known as the Chance or Claus-Chance process:

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$

Calcium sulphide can be prepared by the reduction of gypsum. Another method of preparing hydrogen sulphide consists in passing sulphur vapor, mixed with excess hydrogen or a hydrocarbon gas, through a heated zone.

The greatest objection to hydrogen sulphide, outside of the cost of chemicals, is its bad effect on workmen. It is not only poisonous but small amounts seriously affect the nerves.

Sodium Sulphide was chosen as a more promising reagent for commercial sulphidizing. The results contained in Table II will show that it is much better adapted to the purpose.

The ore from the Shattuck-Arizona mine, at Bisbee, has given the best results. As can be seen from the analysis of the head sample, this ore contains lead, silver, and gold. It is possible to get good recoveries of the metals in a high-grade concentrate

by the application of only a few pounds of sodium sulphide per ton of ore. In test No. 4 the ore (crushed to pass 80-mesh) was treated for 2.66 hours with an equal weight of 1% solution of sodium sulphide or 20 lb. Na_2S per ton of ore. The concentrate collected practically all of the lead in a 50.75% lead product containing almost all of the silver and gold. Theoretically, an ore containing 15.42% lead will require 116 lb. sodium sulphide to convert all of the lead into the sulphide form. As this ore contains no sulphur and only 20 lb. of sodium sulphide per ton was used on it, we have good proof that the lead-carbonate particles are being converted only superficially into the sulphide of lead by the solution of sodium sulphide. In other words, we have true "sulphide filming." Since making the tests in Table II

Table II

Sodium Sulphide solutions for sulphidizing.

Ore from Shattuck-Arizona mine. 500 gm. per test. 15.42% lead, 12.88 oz. silver, and 0.05 oz. gold per ton

No.	Sodium Sulphide	Hours	Flotation oil lb. per ton	Froth. Analyses, and Recoveries.						
				Lead		Silver		Gold	Insoluble	Iron
				Assay %	Recovery %	Assay oz.	Recovery %	Assay oz.	%	%
1	5 lbs. per ton in 0.25% sol.	2.0	Refined turpentine, 0.4 lb. Hardwood-creosote, 1.2 " Eucalyptus, 0.2 "	34.5	34.9	43.10	51.8	0.14	44.6	3.1
2	10 " " " 0.5 % "	2.0	Same	37.3	83.2	38.70	88.9	0.10	43.8	3.3
3	15 " " " 0.75 % "	2.0	Same	38.1	84.8	32.26	86.3	0.10	44.0	3.6
4	20 " " " 1.00 % "	2.66	Refined turpentine, 0.3 lb. Hardwood-creosote, 0.9 "	50.35	97.75	39.82	88.8	0.14	29.6	3.5
5	40 " " " 2.00 % "	1.5	Creosote, 1.40 lb. Turpentine, 0.24 " Pine-oil, 0.08 "	70.1	96.25	58.34	93.5	0.22	6.4	1.27

a mill-run has given equally successful results with the use of as low as two pounds of sodium sulphide per ton and a time of contact with the ore of only a few minutes.

In Table III are two similar series of tests on ore from the Scranton mine in the North Tintic district of Utah, and from the Wilbert mine, in the Dome district of Idaho. While the Scranton ore gives excellent black froth of good grade and a high recovery, it is difficult to do anything with the Wilbert. The reason for this was never quite apparent.

In Table IV is shown the effect of time of contact when sulphidizing with sodium sulphide. A short period seems satisfactory. Further time decreases the recovery, leaving the grade of the concentrate unaffected. In test No. 8, an oil that had

been boiled with sulphur, until its smell became noticeably bad, gave little better results than in other tests in which it was not used.

Table III

Sulphidizing with Sodium Sulphide
Scranton Ore. (No. 1, 2, 3, 4.)
Wilbert mill-dump. (No. 5, 6, 7, 8.)

No.	Sodium Sulphide	Hours	Oil; pounds per ton.	Lead	
				Assay %	Recovery %
1	12 lbs. per ton in 0.6 % sol.	½	Mixture of refined turpentine 0.2 lb., and coal-tar creosote 1.0 lb.	65.5	88.7
2	20 " " " 1.0% "	1½	Coal-creosote, 0.36 lb. Cedar-oil, 0.36 lb.	29.5	90.4
3	40 " 2.0 % "	2	Mixture of coal-tar creosote 1.2 lbs; and refined turpentine, 0.2 lb.	53.7	91.2
4	40 " " 2.0 % "	1	Mixture of cedar-oil, refined turpentine, coal-tar creosote, and rosin; 2 lbs.	66.6	84.3
5	5 " " ¼%	18	Mixture of crude coal-tar, 1.5 lbs. No. 1580 special pine-oil, 0.6 lb.	16.5	52.4
6	10 " " " ½% "	18	Special pine-tar oil, 0.6 lb.	27.3	31.3
7	10 " " ½% "	3½	Mixture of refined turpentine, 0.2 lb.; and crude coal-tar creosote 1.0 lb.	33.15	79.4
8	20 " " " 1.0% "	2	Mixture of turpentine and S_2Cl_2, 0.8 lb., and crude coal-tar creosote, 0.8 lb.	27.2	57.2

In another test the ore was agitated with sodium sulphide in a Pachuca. This test proved that the air oxidized the sodium sulphide to sodium sulphate with but little sulphidizing of the ore, and on further treatment the sulphidized ore re-oxidized.

Table IV

Sodium Sulphide Sulphidizing
Bullion Beck slime-dump. 5.5% lead, 7.2 oz. Silver, 0.02 oz. Gold.

No.	Sodium sulphide	Hours	Oil, pounds per ton	Froth, Analyses and Recoveries.					
				Lead		Silver		Gold	
				Assay %	Recovery %	Assay oz.	Recovery %	Assay oz.	Recovery %
1	20 lbs. per ton in 1% sol.	0.5	Turpentine, 1.0	34.2	74.7	21.8	36.4		
2	" " " " " "	1.0	" "	35.0	44.5	28.1	27.3		
3	" " " " " "	1.5	" "	30.8	41.4	35.9	36.9		
4	" " " " " "	2.0	" "	36.4	46.3	29.5	36.7		
5	" " " " " "	4.0	" "	34.6	37.7	28.2	23.5		
6	" " " " " "	16.5	" "	33.0	59.4	26.2	36.0		
7	" " " " " "	17.0	Creosote, 1.6	19.4	62.4	18.7	46.0		
8	40 " " " 2% "	17.0	Pine-needle oil saturated with sulphur, 1.2	27.0	68.7	27.8	54.2		
9	100 " " " 5% "	88.0	Creosote, 1.6	20.0	63.0	19.4	46.6	0.07	60.6
10	20 " " " 1% "	88.8	Turpentine, 1.2	13.1	70.0	13.4	54.5	0.05	73.0
11	" " " " " "	17.0	Creosote, 1.6	19.4	62.4	18.7	46.0		

Hence it seems imperative that the treatment with sodium-sulphide solution must be without any admixture of air. The simplest machine in which agitation of the relatively coarsely ground ore with sodium-sulphide solution could take place without having an excess of air beaten into pulp, would be a long

rotating cylinder like a cement-kiln, rotated only fast enough to turn over the charge gently without entraining air.

Table V contains the average results obtained in testing various other ores. It can be seen that some ores are not adapted to the process of sulphidizing with sodium sulphide, followed by flotation. The ores that give a poor recovery contain notable amounts of acid-soluble alumina, which makes them clay-like. A number of ores failed to give any results at all—notably the slime from the test-mill of the Copper Queen Consolidated, whose ore has a different geologic association from that of the Shattuck-Arizona. A highly colloidal slime from the mill of

Table V

Sodium Sulphide Sulphidizing

Miscellaneous ores. Average results.

Ore				Concentrates			Recovery			Sodium Sulphide	Time
Mine	Analysis										
	Pb.	Ag.	Au.	Pb.	Ag.	Au.	Pb.	Ag.	Au.		
	%	oz.	oz.	%	oz.	oz.	%	%	%	lbs. per ton	Hours
Chief Consolidated, Utah.	2·8	8·0		8·7	31·9		68	45		10	3·5
Eureka Hill dump, Utah.	2·0	4·7	0·02	14·0	16·9	0·07	40	20	30	20	20·0
American Flag, Utah.	4·2	18·12	0·19	27·1	216·0	1·33	43	48	40	12½	3·0
Bullionville dump, Nevada.	9·87	11·12	0·10	35·9	14·8	0·16	63	46	40	6	2·0
Dry Valley dump, Nevada.	7·12	10·04	0·10	57·8	23·2	0·10	76	27	34	20	5·0
Yellow Pine, Nevada.	15·04	11·92		48·3	29·64		89·2	51·7		20	1·25
Ontario dump, Utah.	4·92	9·44	0·06	32·5	35·78	0·22	62	45	29	20	2·0
Daly West dump, Utah.	5·25	21·8	0·02	9·27	58·70	0·02	15	44		20	2·0

the Mine La Motte, in Missouri, is also difficult to treat. Most of these refractory ores will not even turn black with amounts of sodium sulphide that have been successful on other ores. Whether alumina reacts with sodium sulphide to form aluminates, leaving the sulphur in the elemental condition, is not known, but this might afford a reasonable explanation. Ores containing manganese di-oxide or basic sulphates of iron also consume sodium sulphide without allowing blackening of the lead carbonate.

Sodium sulphide normally costs $30 to $40 per ton at Chicago. With a consumption of 5 to 20 lb. per ton of ore it can be seen that the cost of such sulphidizing is not prohibitive. In fact, it is necessary to decant some of the solution before flotation and

we have often found that not all of the sodium sulphide applied to the ore has been consumed, although the tables of results give the sulphide applied to the ore. Hence the figures given in the tables are probably the maximum possible consumptions and might be considerably reduced in practice by decanting the excess of unused solution before flotation, or by using less sodium sulphide in sulphidizing. This suggests a method of sulphidizing by use of some such device as a thickener where the overflow solution containing sodium sulphide can be returned to the feed of the thickener, together with a small amount of a strong solution of new sodium sulphide. We have determined that if over 0.3% of alkalinity due to Na_2S is left in the water in which the sulphidized ore is suspended, the froth is too tough or else it is entirely killed. Hence, the desirability of decanting the excess of sodium-sulphide solution, and re-pulping with fresh water. We have tested the overflow solution of sodium sulphide for sulphidizing new ore and often find it efficient.

Sodium sulphide may be prepared for large-scale use by the reduction of sodium sulphate with carbon. This is the usual commercial method. The largest use of sodium sulphide at the present time is probably in the tanning industry. When prepared for shipment it is usually in crystals containing a considerable amount of water of crystallization to prevent spontaneous combustion. Hence the market brands of "60%" and "30%" usually consist of only 60% or 30% Na_2S and the remainder is mostly water.

The poly-sulphides of sodium did not prove as efficient for sulphidizing, whereas the sulph-hydrate of sodium, NaSH, seemed to be somewhat more efficient. The normal sulphide of sodium hydrolyzes to sodium sulph-hydrate and sodium hydroxide, and the activity of sodium sulphide is, for that reason, probably exactly the same as that of the sulph-hydrate, although the presence of the sodium hydroxide from hydrolysis might have some effect on the efficiency of sulphidizing. The poly-sulphides of sodium can be prepared commercially by boiling caustic soda with powdered sulphur and probably consist of mixtures of Na_2S_4 and Na_2S_5. We hazard the guess that only

one of the sulphur atoms in these complex molecules is acting as a sulphide sulphur, the others being liberated as free sulphur, for the reason that some of the tests showed white colloidal sulphur lining the bubbles of froth.

In consequence of the above mentioned test-work, carried on at the University of Utah, the Prince Consolidated Mining Company, of Pioche, Nevada, tested the process further in its application of two old pan-amalgamation tailing-dumps at Bullionville and Dry Valley. It was found that practically all of the finely powdered lead carbonate in the ore could be extracted, together with a portion of the silver and gold present. This resulted in the erection of a 300-ton mill. The ore contained about 8.2% lead and 11 oz. silver per ton, together with about $1.40 worth of gold per ton. The finely ground tailing is excavated from the old marsh where it has lain for about 20 years and is then passed through a tube-mill to break up the lumps. It is sulphidized in a round wooden tank with about 7 lb. of sodium sulphide per ton. The agitator in this sulphidizing tank is the regular square-shaft square-arm agitator used in a number of Nevada cyanide-mills and was introduced by the engineer, C. F. Sherwood, who designed the mill. This was installed after the regular Trent agitator (minus the air, not wishing to oxidize sodium sulphide and the ore with air before flotation) had failed to give satisfactory sulphidizing. About one half-hour in the sulphidizer is the minimum time. The ore is then treated for flotation in Callow cells, making a concentrate containing 55% lead.

The recoveries are: lead over 90%, gold 45%, silver 35%. The tailing from the six Callow roughing-cells is separated in a Dorr classifier into sand and slime. The sand is treated on four Deister tables and the slime is mixed with more oil and more sodium sulphide and then passed through two Callow cells, which make a middling concentrate and a finished tailing. The middling is re-treated with the original feed.

After a short time the feed of the mill began to contain many weeds from the old roots that had accumulated from the growth of vegetation during the 20 years. The froth was spoiled and

not until some sulphuric acid was added and the pulp warmed did it return. The present practice is to add sodium sulphide and sulphuric acid together in the agitator, and the mill is at the present time just commencing to operate after the correction of these various unforeseen difficulties. The concentrate contains only about 15 to 20% of insoluble but on being thickened in a Dorr tank and filtered in an Oliver filter it still contains about 26% of moisture. A part of this moisture is removed in a dryer before shipment.

The Shattuck-Arizona Copper Co. is now preparing to build a similar mill for treatment of its ores.

The work at the Shattuck caused a company at Kellogg, Idaho, to take up similar work on a local lead-carbonate ore. It was found that it could be treated successfully and a 40-ton plant is now in operation. The consumption of sodium sulphide is occasionally as low as 2 to 3 lb. per ton. R. S. Handy is responsible for the success of this work.

Calcium Sulphides are more sluggish in their action than the corresponding sulphides of sodium. Again we find the sulphhydrate of calcium more active than the sulphide, which in turn is more active than the poly-sulphide. But for ease of preparation at the mill the poly-sulphide takes precedence. It is obtained by boiling slaked lime with powdered sulphur for two to five hours and is extremely soluble, while the normal sulphide of calcium is only slightly soluble. The normal sulphide can be obtained by reducing gypsum with carbon at high temperature.

The results of a few tests with the poly-sulphide on the May Day ore (Tintic district) are contained in Table VI. The work done with sodium sulphide is superior to that done with calcium sulphide. There are places where the use of calcium poly-sulphide might be advantageous or even necessary, either alone or in combination with sodium sulphide. Some slimes are deflocculated by sodium sulphide so that it is difficult to make them settle. The use of calcium poly-sulphide will have the opposite effect and the proper mixture of the two might be used to control the settling of the sulphidized slime.

The other methods of sulphidizing, such as the use of sulphur

vapor on heated ore, colloidal sulphur solutions, and sulphuretted flotation-oil, have not proved technically successful or adaptable, according to our experiments with lead-carbonate ores.

Oxidized Copper Ores.—Many attempts have been made, both by large operating companies and by other experimenters, to float the carbonate and other oxidized minerals of copper. For that reason the testing of such ores by us has been limited.

Hydrogen sulphide seems to be by far the best medium for sulphidizing oxidized copper ores previous to flotation. When applied to the dry ores we found the same conditions as those

Table VI.

Sulphidizing with solutions of Calcium Poly-sulphide. May Day ore. 4.5% lead, and 2.8 oz. silver per ton. Oils: coal-creosote, 1.2 lbs. per ton; turpentine, 0.4 lb. per ton.

No.	Calcium Poly-sulphide (pounds per ton)	Hours	Froth			
			Lead		Silver	
			Assay %	Recovery %	Assay oz.	Recovery %
1	1.6	6	12.5	32.2		
2	8.0	1.5	18.4	20.7		
3	16.0	3.6	26.1	73.0	11.56	48

mentioned for lead; the particles are sulphidized to the centre, which requires an excessive amount of hydrogen sulphide. Applied to the wet pulp, the hydrogen sulphide seems to cause true filming. Our work has yielded a black concentrate, but we are informed by J. M. Callow, of the General Engineering Co., that the company has been able to reduce the amount of sulphur used to a point where the froth is green with slightly coated malachite. He states that as little as half a pound of sulphur per ton of ore is giving good extractions in the plant of the Magma Copper Co., at Magma, Arizona, where his company has put in the first successful plant of this kind.

Sodium sulphide has been tested by a number of the larger companies that have oxidized copper minerals in their sulphide

ores. The amount of oxidized copper in such ores is usually a fraction of 1%, so that only two or three pounds of sodium sulphide per ton of ore is necessary. This is usually added to the machines during flotation, or to the mixing-tanks before flotation. Our experience is that if some little time of preliminary contact is allowed before flotation is attempted, better sulphidizing of the material will result.

Calcium poly-sulphide has been used for some time in a number of the large copper-concentrating mills with indifferent success, and seems to be detrimental in some instances. On the ores tested by us fair results were obtained if the calcium poly-sulphide was allowed to act until the ore had become well blackened.

It is stated that sulphur vapor was tested at one of the large plants for flotation of oxidized forms of copper and gave better results than any other methods of sulphidizing. Of course this method has the disadvantage of having to be applied to dried, heated, and finely divided ore.

Sulphuretted oils are being used at a number of plants to supplement other methods of sulphidizing and considerable secrecy is observed as to the technical details of this work. During a recent visit of the Utah section of the American Institute of Mining Engineers to the Arthur mill of the Utah Copper Co., the strong smell in the air elicited the information that the flotation unit of 1000 tons daily capacity was receiving a flotation-oil that had been previously distilled with sulphur.

So far as we are aware colloidal sulphur does not assist in the flotation of oxidized forms of copper. Neither has the silicate of copper been successfully floated by sulphidizing flotation. It will blacken when sulphidized, but it resists flotation. Possibly it still presents a silicate surface rather than a sulphide surface. For this reason, most of the large copper companies in Arizona have been considering the leaching of oxidized copper from their tailing rather than lose the silicate copper that may be present.

Another difficulty has arisen from attempts to recover both the oxidized and sulphide copper simultaneously from partly oxidized ores. Throughout Arizona and New Mexico the larger

companies have attempted sulphidizing of the oxidized copper followed by flotation of the natural and the artificial sulphides together. In almost every case they have failed because the flotation of the natural sulphides seems to be spoiled by the conditions that are best for the artificial sulphides. A similar experience is recorded by the Anaconda Copper Co. Only at Chino has this difficulty been mastered, through the efforts of O. Wiser. The product being treated is the vanner-concentrate, which contains considerable oxidized copper. It is, of course, desirable to clean the vanner-concentrate in order to put the iron and silica into a self-fluxing ratio for the smelter. This could not be done if the oxidized copper could not be floated. At first, the sulphidizing reagents caused the natural sulphides to drop out of the froth in this plant, as in many others, and for a time the natural sulphides were floated out first before the sulphidizing reagents were added, but finally the proper mixture of chemical and oil was found to float them simultaneously. One of the principal ingredients is a solution of sodium resinate prepared by dissolving resin in a solution of caustic soda. This stiffens the froth. The froth is red with magnetite and hematite, which float with the copper minerals. The sodium resinate solution is used at several mills.

The plant at Chino is further along in the successful treatment of semi-oxidized copper ores than any of the other mills in the Southwest. Sulphidizing of the whole mill-feed is not yet allowable on account of the large quantities of sulphidizers necessary. Only the vanner-concentrate is being sulphidized with sodium sulphide. However, an experimental unit of one to two tons capacity is also used. The crushed ore for this testing-plant is tube-milled and then tabled to remove the coarse concentrate; after that it is treated in an agitator with sulphuric acid amounting to 3 lb. per pound of oxidized copper present. This dissolves all the copper, including the silicate. On passing the pulp through a ball-mill filled with scrap-iron the copper in solution is cemented and issues with the pulp from the tube-mill. The greater portion of the copper is now ready for flotation without any oiling. The smell of hydrogen is strong and it is the

opinion of the metallurgist in charge that the reaction of the acid on the iron liberates hydrogen and hydro-carbons from the cast-iron used and that these hydro-carbons are partly oiling the cement copper formed. However, on passing to the flotation machine some tar and coal-creosote are necessary in order to get a high extraction of the natural sulphides and the cement copper together. It is said that trouble was experienced in getting a good froth with this material.

This process is being considered by others, notably the Miami and the Inspiration companies. It has been patented by Dr. Rudolf Gahl in U. S. 1,217,437.

One question to be considered in the use of such a process is whether or not substances like iron sulphate will accumulate in the solution to a point where they will injure flotation. It is known that a small amount of ferrous sulphate or of copper sulphate in solution is deleterious. As most of the Arizona mills find it necessary to operate in closed circuit this question of contamination of mill-water is important. It is not impossible that the addition of a little lime to the tailing, as it flows from the mill, would throw out most of the iron and other metals so that the water returned from the tailing-pond would not be contaminated.

The Detroit Copper Co. is known to be experimenting with sulphide-filming of copper carbonate ores. A visit to the test-mill at Bisbee showed an acid-tower used for the preparation of a solution of hydrogen sulphide, which was generated from iron matte and sulphuric acid. The copper ore was being treated with this solution, in round tanks with mechanical agitators, for a number of hours before passing to the flotation machines of the Rork-Kraut-Kollberg type. Laboratory work had previously shown an excellent recovery and the details of larger-scale practice were being worked out at the time of the visit (September 20, 1916).

An interesting paper by M. H. Thornberry was published in the Bulletin of the Rolla School of Mines, Vol. 3, No. 1. A soap, called naphtha powder, manufactured by Peet Bros., was used at the rate of two pounds per ton of ore, with a 6.5 : 1 water:

solid ratio. A minute amount of oleic acid was added. The ore contained both sulphides and oxidized minerals of copper and assayed 2.95% total copper, of which 2.34% was oxidized.

A number of Thornberry's tests, re-calculated to eliminate losses of weight, show the following recoveries when treated by flotation under the above conditions:

Test.	Percentages of Recovery.		
	Oxidized.	Sulphide.	Total Copper.
4.....	61.0	92.1	72.1
5.....	63.8	93.0	75.1
6.....	68.7	89.6	76.6

He offered the following conclusions:

(1) With rain or distilled water this process can be used to advantage.

(2) Water containing sulphates will prevent carbonates from floating.

(3) Water containing chlorides will prevent the carbonates from floating, but this difficulty can be overcome by the addition of sodium carbonate.

Thornberry is the only person who has reported much success with the use of soaps in the flotation of sulphide ores. It is possible that different effects are involved when oxidized ores are considered. Evidence is accumulating to show that it is possible to make certain organic acids form combinations with heavy metals present as carbonates in the ore. The soap is known to hydrolyze in dilute solutions and it is entirely possible that the liberated fatty acids have combined superficially with the copper-carbonate particles sufficiently to "oil" them for flotation. The use of sodium resinate in the flotation of copper carbonates at Chino has already been mentioned. Sodium resinate is nothing but a resin-soap. The resin acids are not so well known to metallurgists as are oleic, palmitic, stearic, and other acids, whose sodium salts form the principal ingredients of soap. A study of the action of these organic acids on minerals is desirable.

Oxidized Zinc Minerals.—So far as we know no one is successful in the flotation of oxidized ores of zinc. Our results are absolutely negative. We are informed that some headway was made with the problem by F. W. Traphagen and one of his students, at the Colorado School of Mines, but the sulphide film seemed to come off easily. Poor results were obtained, whatever the cause. Only Bacon claims any success in this line and his method is to get the zinc into solution in, say, the sulphate form, followed by precipitation of zinc sulphide by the use of an alkaline sulphide, with subsequent flotation from the sulphidized pulp—at least his patent claims as much. There are few places, however, where sulphuric acid and sodium or calcium sulphides could be obtained cheaply enough to allow of the application of this process.

We have recently been informed by Frank A. Bird, of Salt Lake City, that he has obtained some success in the flotation of a zinc-carbonate ore, by using the idea seemingly underlying Thornberry's work. After many of the ordinary flotation-oils had failed to do anything with sulphidized or non-sulphidized ore, oleic acid was added to an ore-sample while being sulphidized with sodium sulphide. The result was a fair grade of concentrate and about 50% recovery. Whether the sulphur in the sodium sulphide had anything to do with it or whether alkalinity was all that was necessary, was not determined.

Other Minerals.—Flotation on a commercial scale seems to be possible only after sulphidizing. We are not certain but that cuprite and similar minerals of highly developed cleavage or crystalline character can be floated direct without sulphidizing. From private parties we hear of laboratory successes in the flotation of scheelite, fluorite, and similar minerals. The flotation of magnetite seems well established.

FLOTATION AT COBALT, ONTARIO[1]

By W. E. Simpson

Synopsis.—Flotation has proved a useful auxiliary in the treatment of silver ores, and is now in operation at practically every producing mine in the Cobalt district. Mines originally equipped with plants for gravity concentration have bettered their recovery as much as 5 to 15% through the addition of flotation-units, while the added cost is from 5 to 15 cents per ton. With the all-sliming process (grinding in cyanide solution), extensive experiments indicate that when recovering the refractory minerals by flotation, the usual revenue is maintained or improved, and that the consumption of cyanide is reduced one-third. The chief difficulty with flotation lies in the disposal of the concentrate, marketing to distant smelters being expensive and local treatment not yet having proved satisfactory. Threatened litigation by Minerals Separation, Ltd., is also seriously embarrassing metallurgical progress in the Cobalt district.

History.—The earliest application of the flotation process to the treatment of silver ores at Cobalt dates from 1910, when some small-scale tests were made in the laboratory at the Coniagas mine, to note the effect, if any, of violently shaking representative samples of mill-pulp to which had been added a few drops of oil. No commercial importance was attached to the results obtained in these simple experiments and the matter remained in abeyance so far as that mine was concerned until quite recently.

The next attempt was made in 1914, when a former employee of the Minerals Separation company constructed an experimental unit at the Temiskaming mine and demonstrated the feasi-

[1] From the *Mining and Scientific Press* of December 8, 1917.

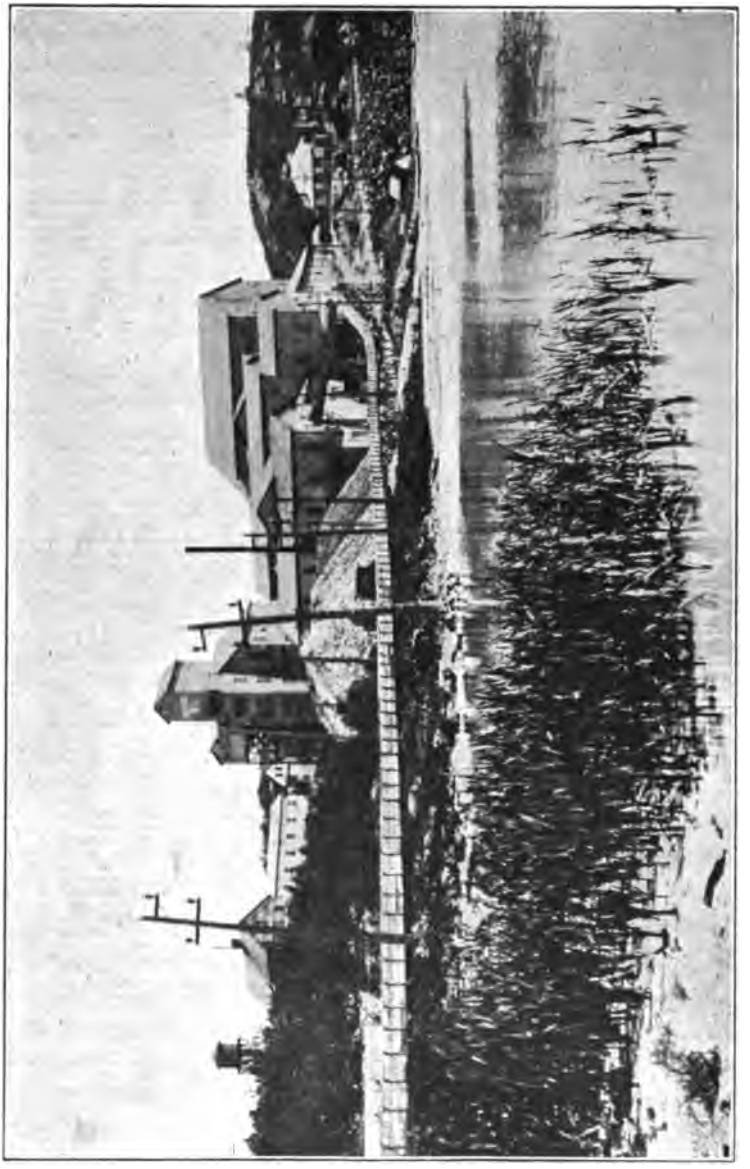


FIG. 1.—The Dominion Reduction Works, at Cobalt, Using the Callow Flotation System

bility of profitably treating the fine tailing, then being run from the concentrating mill to the waste-pile. The litigation ensuing over the use of flotation acted as a deterrent to the continuance of experiments.

While these tests were being conducted, a sample of slime, representative of what may be now called flotation-feed, was sent by the Cobalt Reduction Co. to its consulting engineer in London to determine whether the flotation process could be introduced successfully in the Cobalt district. The tests were made in the laboratory of Sulman & Picard, metallurgists for Minerals Separation, Ltd., and the results were as follows: The sample assayed 5.5 oz. silver per ton, and the products obtained were a concentrate assaying 43.5 oz. containing 57.11% of the silver in 7.3% of the weight of the original slime, a final tailing assaying 1.99 oz. per ton with 24.88% of the gross content left in 69.15% by weight of the slime, and a middling containing the rest. Alf. Tellman, who signed the report, concluded by saying: "I believe that if the slime can be successfully treated by cyanide you will be able to make more profit than with flotation."

The serious adaptation of the flotation process to the Cobalt ores really started when T. R. Jones, manager of the Buffalo Mines, after conducting an extensive experimental campaign, installed the first treatment plant to operate on a commerical scale in October, 1915. This unit employed the Callow type of machine and had a capacity of from 50 to 75 tons per day. So satisfactory were the results that additional plant was immediately erected, bringing the total capacity to 600 tons per day in September, 1916.

The first flush of success led to the statement by enthusiastic operators that flotation would entirely replace the gravity method of concentration, completely displace the cyanidation of Cobalt ores, and revolutionize the established practice of metallurgy. Further experience, however, has called for a modification of these views. A satisfactory recovery of the silver-bearing minerals by flotation is only obtainable from material in a fine state of subdivision and the tendency now is to apply the process to the treatment of slime and to such portions of tailing

as may be sufficiently rich to warrant the additional expense of fine grinding.

The Ore.—The Cobalt orebodies are aggregations of veins formed, apparently, by the deposition in regular succession of various minerals in zones of fracture in the country-rock, which may be either slate or conglomerate. No actual walls define the limits of these orebodies, but the gross width of mineral matter extractable at a profit may reach 20 or 30 ft., although the veins individually are seldom more than a few inches wide. A geological diagnosis indicates the deposition of the minerals in the following sequence: Smaltite, niccolite, calcite, argentite, native silver, and, lastly, bismuth; copper also occurs in traces. The ore, therefore, is decidely complex.

About 90% of the silver of the district occurs in the form of the native metal, a fact that did much to simplify metallurgical operations in the early days, and permitted many mining prospects to develop into wealthy producers without any capital outlay beyond that required for the purchase of a few tools. This metallic silver frequently is found in slabs six to eight inches thick and weighing thousands of ounces, but much of it occurs in a state of subdivision so minute as to necessitate pulverization of the ore to pass a 200-mesh screen in order to obtain a satisfactory extraction. According to laboratory experiments by J. M. Callow and E. B. Thornhill [2] this fine native silver floats more readily than any other silver-bearing mineral. Actual full-scale work in the mills, however, fails to support this statement.

Early Milling.—The first mills erected at Cobalt were equipped with crushers, stamps or rolls, jigs, and gravity tables, two products being obtained, a concentrate assaying several thousand ounces per ton, that was sold to the smelters, and a tailing that was stored and is now the principal material available for treatment by the flotation process. Later plants were equipped for both gravity concentration and treatment by cyanide. At this date (October, 1917), owing to the success achieved by the Buffalo Mines, every mill is either equipped with a flotation annex or has one under consideration.

[2] Bull. Can. Min. Inst., June, 1917.

Applicability of Flotation.—In reaching a decision regarding the adoption of a process and the installation of a plant, two factors exert an influence in favor of flotation at Cobalt more than in mining districts generally; these are (1) the winter is long and heating is costly, and (2) many of the mines appear to have already passed the zenith of their prosperity, their ore-reserves being now narrowly limited in extent. The most desirable process for the Cobalt mines, therefore, is one that can be housed in the smallest building and installed with the lowest capital outlay. Experience has proved that a flotation plant can be erected in a space less than one-fourth that required for either a group of gravity-tables or a cyanide-plant of equal capacity. In a modern mill for treating 100 tons per day it is estimated that a saving in capital expenditure of about $20,000 can be effected by the substitution of the new for either of the older methods. The working profit also favors the newer method. The chief handicap to flotation is its inability to produce a finished article, that is, one easily marketable, such as high-grade bullion. Flotation in reality is a method for concentrating valuable mineral into small bulk, the ratio of the weight of material treated to that of the product being, in the Cobalt district, approximately between 50 and 100 to 1. This concentrate either must be treated locally or sold to distant smelters, whereas if cyanide bullion is produced no further treatment is necessary.

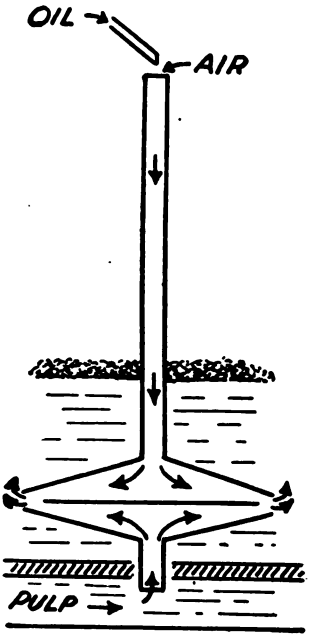


FIG. 2.—The Groch Impeller

Flotation-Oils.—Owing to the difficulty in floating the arsenides and other refractory minerals with which the silver is associated, the oil-mixture to be used must fulfil the conditions of

being a collector, a frother, and a powerful adhesive. The Cobalt blend of oil consists of 20% pine-oil, 70% cresote, and 10% tar. The last does not have the selective action on the valuable minerals that could be desired, its function being to adhere tenaciously to the mineral and improve the recovery, although this is at the expense of the grade of the concentrate produced. The consumption of oil throughout the district varies from ½ lb. to 2 lb. per ton of material treated.

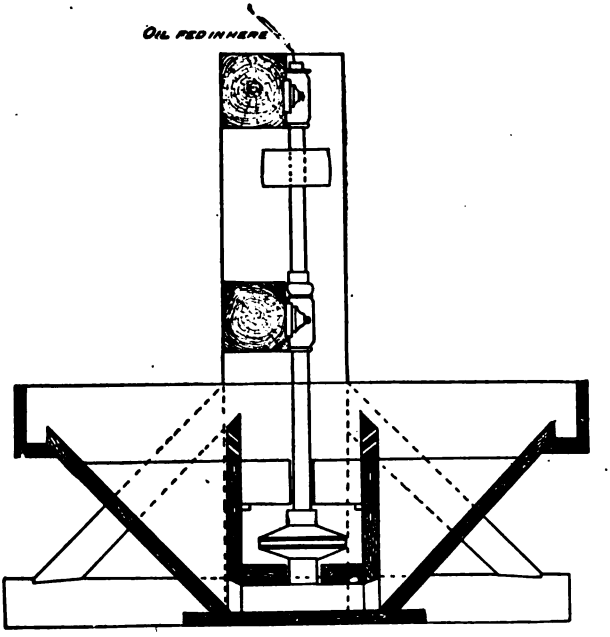


FIG. 3.—The Groch Flotation Machine

Flotation Appliances.—The Callow system of flotation was the first to operate commercially in the district, and, as the results obtained were satisfactory, the pneumatic cell rapidly became popular. The Callow appliance has been so often described that a repetition here is unnecessary. Recently a machine, the invention of a local engineer, F. O. Groch, has made its appearance, and indications are that it possesses merits that should entitle it to consideration. Externally it bears a striking re-

semblance to the Minerals Separation machine, but the method of operating is quite different. It may be described as a number of impellers operating in a V-box 14 ft. long by 5 ft. wide, divided transversely and longitudinally into compartments, the partitions being slotted or submerged so as to compel the pulp to take

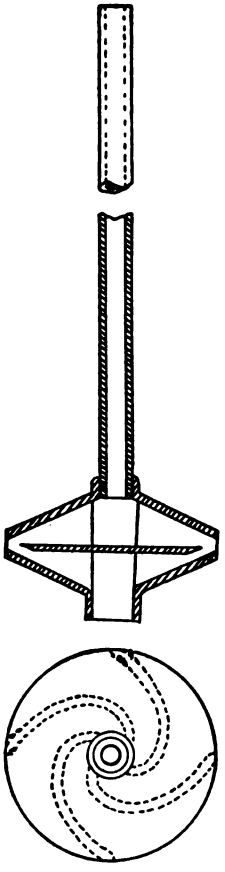


FIG. 4.—The Groch Impeller.

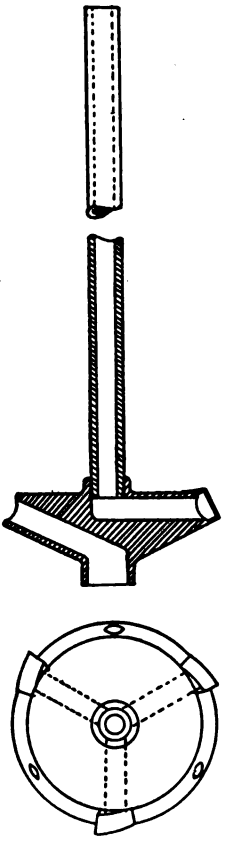


FIG. 5.—The Ruth Impeller.

a zigzag course, both vertically and horizontally, in its passage through the machine. The impellers, six in number, combine the functions of centrifugally agitating the pulp, diffusing the oil, and sucking air into the mass during agitation, all accomplished in one operation. The impeller consists of a hollow

panies of approximately $40 to $50 per ton of concentrate exported. Assuming a concentrate assaying 500 oz., with silver at 70c. per oz., based on shipment from Cobalt to Denver, the details of cost are as follows:

		Per ton of concentrate
Steam-drying to approximately 10% moisture, coal at $7.50 per ton		$2.50
Sacking and loading		1.35
Sacks and wire-ties (allowing five trips per sack; original cost of sack, 15c.)		1.05
Haulage from plant to cars at Cobalt, about		0.75
Freight, Cobalt to Denver		14.20
Treatment-charge at smelter		10.00
Extraction-loss, 5% on 500 oz. silver at 70%		17.50
Incidentals:		
U. S. revenue, per car	$1.20	
Assaying	6.00	
Customs' charge	2.50	
Representative at sampling	7.00	
Total	$16.70	0.42
Total		$47.77

Local Treatment of Concentrate.—Two methods of treatment locally are being tried, the one necessitating roasting of the concentrate, the other operating with this material in its raw state. The roasting process consists in placing the concentrate, with 15% moisture, in a specially constructed furnace, patented by the Holt-Dern organization, where it is slowly oxidized without allowing any flame to reach the surface. The charge is a mixture of gravity and flotation-concentrate in the ratio of 1 : 4, giving a self-roasting mixture, the fuel being supplied from the sulphur, antimony, and arsenic present. The furnace may be described as a 7 by 9-ft. rectangular brick-lined chamber 4½ ft. deep, into which during operation the charge is fed wet at regular intervals, a corresponding amount of the roasted product being simultaneously withdrawn underneath through the patented grate with which the furnace is equipped. Thus a blanket of wet concentrate remains continuously on top, minimizing the loss by dusting and volatilization. The contained moisture is really a saturated solution of common salt from which the chloridizing effect is derived.

The roasted material is leached with brine and the silver precipitated on scrap-copper. The copper is later recovered by precipitation on scrap-iron. The resulting silver, in the form of a cement, is treated with acid and melted.

The cost of this treatment is not yet ascertainable as many difficulties are being experienced that will require ingenuity to overcome. The brine eventually becomes foul and the customary high-grade bullion, which Cobalt operators consider as their standard for export, is not obtainable except at a prohibitive cost for labor and acid.

Leaching by brine may be replaced later by agitation in cyanide solution, thereby eliminating some of the difficulties, but at an increased cost. For this work a thorough roast would be essential and this is scarcely obtainable in any furnace where the charge remains motionless during the whole operation. Results so far indicate that the charge has a tendency to sinter. There remains the alternative of dealing with the concentrate in its unroasted state. Here, as in so many other matters, local metallurgists have shown remarkable enterprise, and hopes are entertained that a process, already installed at the Cobalt Reduction Works for the treatment of gravity concentrate, may prove applicable to the flotation product. This process consists of intensive tube-milling, first in water with 25 lb. of calcium hypochlorite per ton of concentrate treated. The operation exerts an oxidizing and chloridizing effect, which is completed in about 24 hours. Then follows a period of water-washing and agitation in a 0.25% cyanide solution for 48 hours, during which time about 95% of the silver-content is extracted. Filtering then follows, and precipitation from the solution is effected by the sodium-sulphide method with the production of bullion 996 fine.

This method applied to flotation-concentrate has so far failed badly. The oil-mixture used for the recovery of the concentrate is of a decidedly tarry and adhesive character; consequently the difficulty of attacking the oil-enveloped particles with the cyanide is even greater than that experienced generally in dealing with flotation concentrate. A vigorous campaign of experi-

mental research is being started and it is confidently expected that the existing difficulties will be overcome.

Recovery and Cost of Operation.—The litigation, with which the Cobalt district is being threatened, prohibits the publication of authoritative details for fear that they may be used subsequently in law-court proceedings. It may be stated, however, that, as a general rule, the recovery varies from 75 to 90% of the silver in the material treated by flotation and the cost of the actual operations from the time of receiving the slimed feed to that of discharging the finished concentrate is roughly 20c. per ton, divided as follows:

Item	Cents
Oil	4
Labor	9
Power	6
Repairs	1
	20

The estimated cost of treating the accumulated sand-tailing of the Buffalo Mines by flotation, and of converting the concentrate recovered into actual cash, is given in detail by Robert E. Dye in a paper read before the Canadian Mining Institute in March, 1917, together with those obtained in previous operations by sliming in cyanide. The particulars are as follows:

	Flotation, Cents.	Cyanidation, Cents.
Loading tailing by steam-shovel	4	4
Tube-milling and classifying	40	50
Heating and lighting	3	10
Overhead expense	14	14
Thickening, agitating, etc	..	16
Chemicals	..	48
Precipitation and miscellanies	..	17
Refining	..	3
Flotation	8	..
Drying and loading concentrate	5	..
	74	$1.62
Smelter-charge, including freight and losses	83	...
Total, per ton	$1.57	$1.62

A 90% recovery is obtained by flotation, and a similar extraction by cyanidation to which intensive tube-milling is a contributing factor. The working cost for both systems is practically identical, but there are possibilities of reduction in the cost of treating flotation concentrate that do not exist in the competitive method. No charge is shown in the foregoing figures for amortization and depreciation, and as the quantity of material available for treatment at the Buffalo Mines is not over 350,000 tons, the deciding factor of capital expenditure is overwhelmingly in favor of flotation. A promising avenue for research in Cobalt is being found in the endeavor to obtain a combination treatment of sliming in cyanide followed by flotation. It has been discovered that, if the customary strong cyanide solution be used, subsequent treatment by flotation is abortive, and that the flotation recovery is increased as the cyanide solution used in the initial treatment is weakened. The probable reason for this is that strong cyanide, in attacking the silver-bearing minerals, pits their surface, thereby lowering their flotability. Experiment shows that a reduction in the strength of the usual working solution from 0.25% NaCN to 0.10% lowers the extraction by that chemical from the regular 90% to 75% of the silver in the ore, but it leaves the residue in such a state that, with suitable water-washing, a further 75% of the content is readily recoverable by flotation. This modification is showing a saving of over one-third of the cyanide ordinarily consumed.

Minerals Separation.—In harmony with its attitude elsewhere, the Minerals Separation Company, through its subsidiary organization, the North American Corporation, has threatened proceedings against all users of flotation in the Cobalt district, so as to collect, if possible, the royalty of 2½% of the gross value of the whole concentrate recovered, according to the usual demands of this patent-exploiting company. The success of flotation at Cobalt is due entirely to local enterprise, therefore this demand is resented bitterly. The indications are that a legal fight is to follow, and a campaign had been started to enlist Government action " with a view to having the patents annulled." Amid the legal turmoil, metallurgical progress is being seriously

handicapped, the free exchange of ideas has been completely stopped, and an embargo is being placed on valuable information. It is sincerely hoped that an equitable settlement may be obtained at the earliest possible moment.

Conclusion.—Flotation is undoubtedly destined to play a part in all milling operations in the Cobalt district, although its scope will not be as extensive as was at first anticipated. As a competitor to the sand-table it has not met with the success gained in other localities for the reason that the valuable minerals are difficult to float and are easily recoverable by gravity-methods. For successful flotation, the arsenic, nickel, and cobalt minerals, with which much of the silver is associated, must be reduced to a fine state of subdivision in order to conform to some flotation law in which the ratio of surface-area to mass is an important factor. Fine crushing is expensive; consequently the best field for flotation lies in the treatment of primary slime. On this material, it has already completely superseded the slime-table, the additional revenue being greatly in excess of any additional cost incurred. One concentrating plant treating 150 tons of ore per day has been able to add to its recovery from 200 to 300 oz. of silver in concentrate daily, the additional revenue being directly attributable to the introduction of flotation for the treatment of slime. The approved type of gravity mill for Cobalt, therefore, should contain jigs for the extraction of the coarse metallic silver, gravity tables for the treatment of sand, and flotation for the slime.

In the cyanidation of Cobalt ore, certain inroads by flotation have been made, but this results not so much from the actual benefits derived from the use of flotation as from the disadvantages both temporary and permanent associated with the older system. During the War, a shortage of cyanide has been frequently threatened and the finding of some substitute has become imperative. No actual shortage in Canada has, so far, been experienced but the possibility of having to suspend operations for this reason has acted as an incentive to the development of flotation.

Cyanidation lacks elasticity, especially in respect of the cost-

sheet. A fixed consumption of cyanide per ton of ore treated has to be incurred regardless of the value of the material being cyanided. This means practically a fixed limit of cost with no margin for fluctuations in revenue. The ores of Cobalt are notoriously erratic in value, consequently, on many mines, often owing to a fall in grade, cyanidation is actually being conducted at a loss. With flotation, the chief item of cost is directly associated with the treatment of the valuable concentrate produced, consequently the total cost of the whole operation fluctuates directly as the value of the ore being treated. This is a most favorable factor. A combined cyaniding and flotation plant should therefore give an improved recovery, effect a saving in cyanide, and automatically harmonize the cost of treatment with the value of the ore being milled.

Flotation has already been allotted a useful place on practically every producing mine in the district and its sphere of operation is bound to increase greatly as soon as a more advantageous method of disposing of the product has been devised. The probabilities in this matter seem to favor treatment locally.

The capital outlay for a flotation annex, with storage-tanks, filter, buildings, etc., but no crushing appliances, is roughly $50 to $60 per ton of daily capacity. This, in itself, gives the process an advantage over all competitors.

The flotation of silver ores is now a well-established success and the results being obtained from researches in the Cobalt district should prove of much interest to operators in other countries, particularly Old Mexico, where the argentiferous minerals are less refractory and can be much more readily treated than those of New Ontario.

CASCADE METHOD OF FROTH-FLOTATION [1]

By H. Hardy Smith

Modern flotation practice is almost entirely concerned with what is now known as air-froth flotation, and the practice of air-froth flotation is in turn largely concerned with methods of getting atmospheric air into intimate association with a mixture of mineral particles in water. The process therefore can be subdivided according to the manner in which the air is introduced, and at present there are three distinct processes, first, the mechanical agitation or Minerals Separation process, second, the pneumatic or Callow process, and, third, the fluid-jet air-entraining or Cascade process. The last is of recent origin and at present is in use only to a limited extent in comparison with the other two processes. Owing to its intrinsic merit, however, it bids fair to occupy an important position in the metallurgical use of froth.

The Cascade process works by virtue of the fact that a stream or jet of fluid tends to drive or carry contiguous particles of a surrounding fluid along with it, as a result of the friction at the interface caused by the adhesion between the two fluids. This principle was recognized centuries ago, and was applied by means of the " trompa " or hydraulic air-compressor, to supply air at low pressures for the Catalonian forges. About the middle of the last century it was employed in the form of the jet-pump and the jet-ejector, and it also enters into the action of the modern steam-injector.

The extraordinarily large volume of air or gas that can be injected by a jet of water against a moderate resistance by this means, leads to the supposition that the force of adhesion between air and water is greater than had been commonly supposed.

[1] From the *Mining and Scientific Press* of April 13, 1918.

The operation of the hydraulic air-compressor depends primarily on the grip that a rapidly descending surface of water can obtain on the contiguous air, and the high efficiency, which many of these contrivances have shown, is evidence that the forces engaged are not fickle or elusive, but are constant and reliable.

In the Cascade flotation process, the jet or stream of fluid is not only employed to introduce air into the body of the pulp, but its kinetic energy is absorbed also in producing agitation, so as to thoroughly disseminate the bubbles throughout the mass and to assist them in their grasp upon the mineral particles which are to be floated. This agitation is not to be compared in its intensity to that in the method of mechanical agitation, but is more in line with that produced by the pneumatic process.

It is important to distinguish between the kinds of bubbles. In a froth-flotation sense there are active and inactive bubbles. Air introduced into the body of a liquid necessarily must produce bubbles before it escapes at the surface, since a bubble is merely a certain volume of air surrounded by a liquid, but, from a flotation-standpoint, some air will be consumed in forming useful bubbles, and the remainder will escape without performing any useful purpose. For example, a jet of air blown into a pulp free from a frothing contaminant, even if the other flotation conditions are good, will produce mostly inactive bubbles, and even if a frothing-agent be present, the proportion by volume of inactive bubbles will be large. Apparently the activity of a bubble is in inverse proportion to its diameter, but there may be other less obvious factors.

In the so-called pneumatic process of froth-flotation, the enormous production of bubbles for a given result is its most striking characteristic, a point which would lead one to suppose that the proportion of inactive to active bubbles is large, and consequently that the "bubble-efficiency" is low. On the other hand, the froth production for a given result with the Cascade method is decidedly moderate, and consequently the bubble-efficiency must be relatively high. In this respect it probably does not equal the method of mechanical agitation, but the large consumption of energy to produce the bubble and transport it

through the pulp to the surface, in the latter method, is an economic drawback. It will be necessary to learn more about the fundamental physical principles governing the production of bubbles in liquids before it becomes possible to indicate the reason for this high bubble-efficiency inherent in a volume of air injected as a film adhering to a fluid surface in rapid motion; but whatever be the reason, the fact remains that this method of introducing air and of agitating brings about the desired results in a particularly pleasing and efficient manner. The Cascade process is the logical outcome of the growing recognition of the importance of air in froth-flotation practice, since anyone of ordinary intelligence could not stand below a waterfall or a cascade, and observe the intense aeration in the pool beneath, without immediately being struck by the potentialities inherent in this method of agitation, were he cognizant of the fact that in this intense aeration lies the basic principle governing the successful froth-flotation of minerals.

On the economical and practical sides the strong points in favor of the Cascade process are: the simple and inexpensive plant, insignificant wear and tear, low repair-costs, small power-consumption, and the meagre attendance and regulation required to keep the plant running under good conditions. The honor and credit for first recognizing the principles underlying the Cascade process, and for embodying them in practical form, seem to be due to Messrs. Seale and Shellshear, of the Junction North mine at Broken Hill, Australia, where a full-sized working plant was put into operation about the end of 1914. As frequently happens, the same idea was hit upon and developed independently at practically the same time in other widely separated localities, namely at the Arizona Copper Co. in the United States and at the Suan mine in Korea. Later on, in 1916, U. S. patent No. 1,187,772 was taken out by G. E. Ohrn, and another No. 1,202,512 by Gustaf Gröndal, both of Sweden, for apparatus embodying the Cascade principle. About the same time a simple machine of true Cascade type was evolved at the Mineral Farm mill, at Ouray, Colorado. Recently Commonwealth Patent No. 2353/16 was taken out by L. V. Waterhouse, of Mt. Lyell,

Tasmania, for a novel form of the Ohrn machine. Although all the contrivances developed by the various investigators contain the same fundamental principles, the method of application differs widely. With some of the plants it is claimed that violent preliminary agitation and mixing of the flotation reagents with the pulp is unnecessary, but in most cases it will be found that this is highly desirable. The excellent mixing and emulsification which can be obtained by grinding the ore with the reagent in a tube-mill, in certain cases, may be sufficient, but supplementary agitation of the pulp, diluted to a consistence suitable for flotation, will not, in the general run of cases, be found amiss. In the apparatus developed at the Junction North mine, followed by other mines at Broken Hill, and by the Arizona Copper Co., as well as at Suan, and at Mineral Farm, the force of gravity alone is relied upon to inject the air and to disseminate it through the pulp. If insufficient natural fall is available, artificial fall must be created by means of elevators or pumps, which, at the same time, can be relied upon to provide a certain amount of the desirable preliminary mechanical agitation. In the Ohrn and Gröndal forms, the energy of high-pressure steam is employed, and in the Waterhouse machine, that of high-pressure water or solution. In these latter types it is safe to assume that preliminary violent agitation is not so vital, since the energy expended within the machine itself is greater than in the simple gravity-types.

The necessity for providing equalizing apparatus at the head of the plant is even more important in the case of the Cascade process than in other flotation processes, especially with gravity plants, since the nature of their operation makes them very sensitive to fluctuations in the volume of the feed. This lack of flexibility is one of the chief disadvantages of the process. A plant once designed for a certain tonnage, or more correctly, for a certain volume of pulp per unit of time, will not work satisfactorily at points much above or below this volume, and adjustments to suit altered conditions are not readily made.

In certain cases the froth produced in the Cascade process is extremely evanescent, and if allowed to occupy areas approaching

those used with other flotation processes, the result will be failure. Where disappointing results have been obtained in trials with the process, it is fairly safe to assume that this was one of the points not fully comprehended. The ratio of frothing-area to capacity is one of the most important considerations in the design of a plant. On account of the frail froth that is liable to be encountered, another important thing is to provide for short travel and rapid removal of the froth-concentrate. A Cascade machine, in the design of which proper attention has been paid to the above two points, will be found particularly efficient on coarse material, or in preferential flotation. In the case of a relatively high-grade pulp, containing a large proportion of readily floatable sulphide slime, the points mentioned may not be of such importance.

Turning to the mechanical details, Fig. 1 is a diagrammatic sketch of the simplest type of apparatus, and the only one which is accurately described by the name " cascade." Its chief recommendation is its simplicity. The feed-apron spreads the moving liquid into a sheet, and although this gives a large area, it is not the maximum area in contact with air that the same volume of liquid could provide. This would lead to the supposition that the efficiency of the machine is not high. In the one developed at the Mineral Farm mill, not even crowding-boards were employed, the apron simply discharging into a box of square section, and the float being skimmed off continuously by a paddle. The results are said to be quite satisfactory. The capacity of a plant depends on the length of the frothing-boxes and the intensity and time of treatment on the number of steps or cascades. Both can be increased indefinitely, but it is preferable to have not more than six steps in succession, and, if further treatment is necessary, to interpose an elevating device to raise the pulp to the next tier. The frothing-boxes must be properly designed to suit the hydraulic head of each step, otherwise a loss of energy will result. This applies to all types of gravity machines. With the type shown in Fig. 1, a 30 to 40-in. head will usually be sufficient.

A more advanced type of apparatus is represented in Fig. 2. In most cases this could be expected to yield better results than

the arrangement shown in Fig. 1, yet it is open to the objection that it involves more mechanical complication, and there is a loss of head between the steps, in consequence of which the total fall may not be utilized to the greatest advantage in the aerators. The capacity of the plant depends upon the dimensions of the

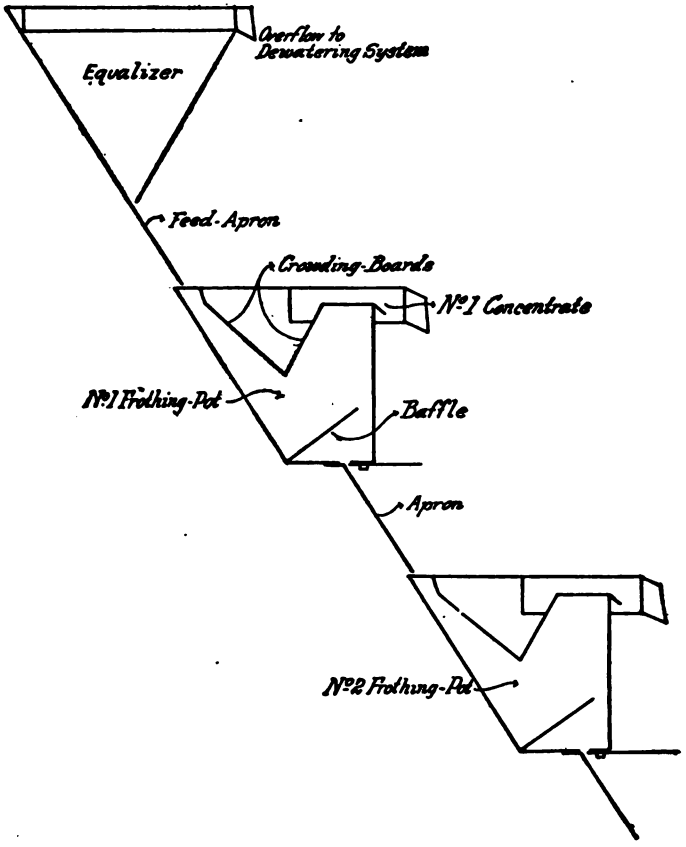


FIG 1.

induction-pipe and the frothing-pot. These cannot be increased indefinitely, so that a multiplication of units is necessary for a large tonnage. Very large volumes of air can be entrained by means of the induction-pipe, either with or without the small air-pipes shown in the aerator in Fig. 2, and this part of the ap-

paratus is undoubtedly efficient both as an aerator and as an agitator, in combination with its bucket or diaphragm. A length of induction-pipe of 25 to 30 inches in the clear will usually give good results, but to get the total height between steps, the loss of head in the aerator (6 to 8 in.) and in the under-flow pipe from the preceding frothing-pot must be added to it. The latter will depend on the density and coarseness of the pulp under treatment,

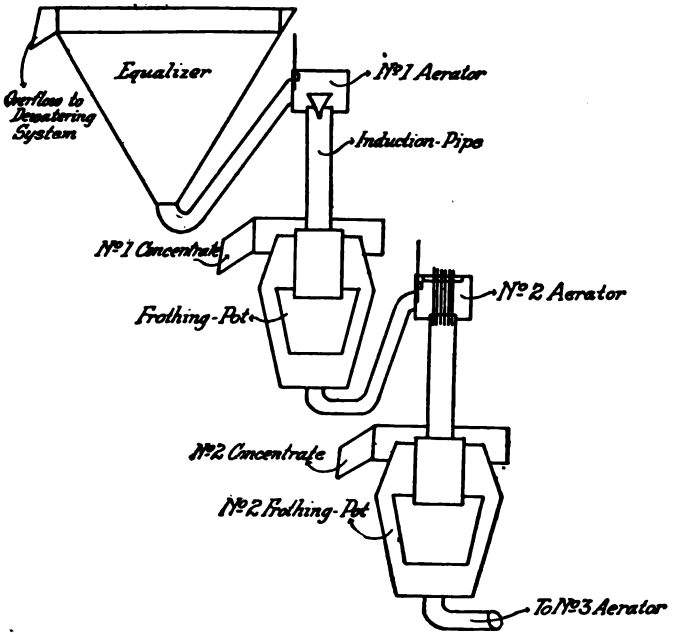


FIG. 2.

but it will usually not be satisfactory at less than 12 in. Individual small frothing-pots have the advantage of providing a rapid discharge for the concentrate, and this apparatus is therefore well adapted to coarse material, to refractory ores, or to preferential flotation. The machines developed at the Junction North mine, Broken Hill, and at the Suan mine, Korea, are of this type.

Another type, corresponding to what was developed at the Arizona Copper Co.'s mill and at the Central mine at Broken

Hill, is shown in Fig. 3. Considerable difference of opinion may arise over the relative merits of the two types represented by Fig. 2 and 3, but as they come into more general use, admitting

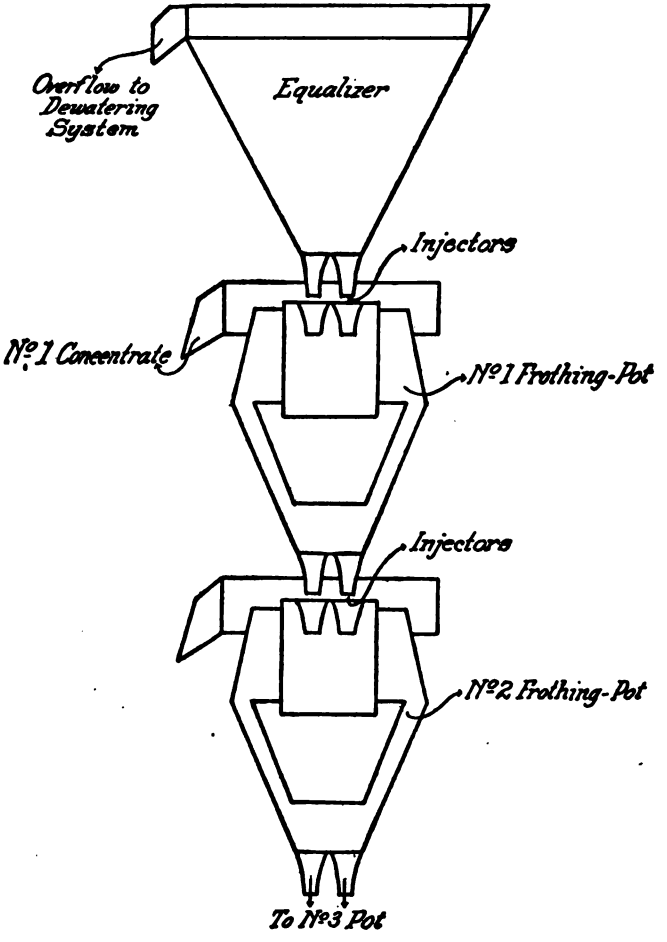


FIG. 3.

the comparison of operating results, doubtless one will become popular at the expense of the other. With two pots working side by side, one fitted with jets and the other with an induction-pipe, although the froth had a different appearance, the amount

of concentrate coming over seemed to be the same. The apparatus shown in Fig. 3 has the advantage of less complication and practically no loss of head, but the jet-injectors must be carefully designed and the nozzle needs frequent renewal. It is found that 30 to 40-in. head, and $\frac{5}{8}$ to 1-in. nozzles, will give satisfaction. When a rapid froth removal is necessary it is desirable to have small individual pots, either of square or round section. Common oil-barrels make satisfactory pots of this class. With many ores, especially where large tonnages have to be treated, oblong pots would be preferable, the length depending on the tonnage that it is desired to treat in each unit. Very long pots are liable to be unsatisfactory on account of the difficulty of distributing the feed evenly.

One of the latest developments in the Cascade type of machine is shown in Fig. 4. It is covered by the Waterhouse patent. A high-pressure liquid jet is used, both to inject air and to agitate the pulp. This machine will doubtless be elaborated and brought to a high state of metallurgical and mechanical efficiency. A pressure of about 80 lb. is used at the jet, and this pressure can be obtained by using a pump, as seen in the sketch. Since only solution and the finest suspended slime pass through the pump, the wear and tear are not excessive. The frothing-pot is made deep, and is fitted with baffles to confine the violent agitation to the lower part of the vessel. The frothing-compartment is usually oblong in shape, and the single pump supplies several jets with high-pressure liquid. To get multiple treatment of the feed, each jet discharges into its individual pocket, which is separated from the succeeding pocket by a partition over which the pulp has to travel in order to reach the final pocket where it is discharged. The flotation reagents should be thoroughly mixed with the pulp before being fed into the separating-tank, since it is preferable that the high-pressure liquid used at the jet should carry its proportion of frothing-agent before injection.

The apparatus shown in Fig. 5 presents a radical change from the preceding types, but its governing principles bring it within the Cascade classification. In this case the stream of fluid that entrains the air and causes the agitation is not a liquid but a

vapor, namely high-pressure steam, the energy of which is utilized by means of a steam-jet injector. On account of the very low thermo-dynamical efficiency of the latter, this machine cannot be economical except when steam has to be used in any case to

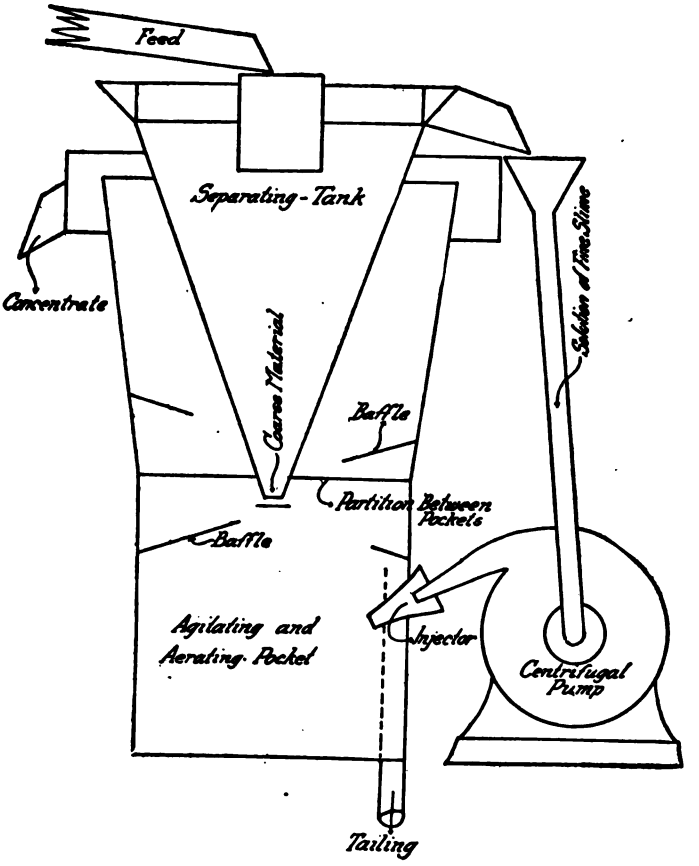


FIG. 4.

heat the pulp. In that special field it has a promising future. Oil is mixed with the steam before it strikes the pulp by being drawn into the jet through the small pipe shown in the sketch. It is claimed that better distribution of the oil is obtained in this way, and the claim is well founded, because the heated and ato-

mized oil should certainly possess great covering power. The jet not only forces in the air for the bubbles, but also injects the pulp into the machine. The exact object of this is not clear, but, in the case of multiple-treatment, it would make it possible to have the series of units on the same level, the tailing from one

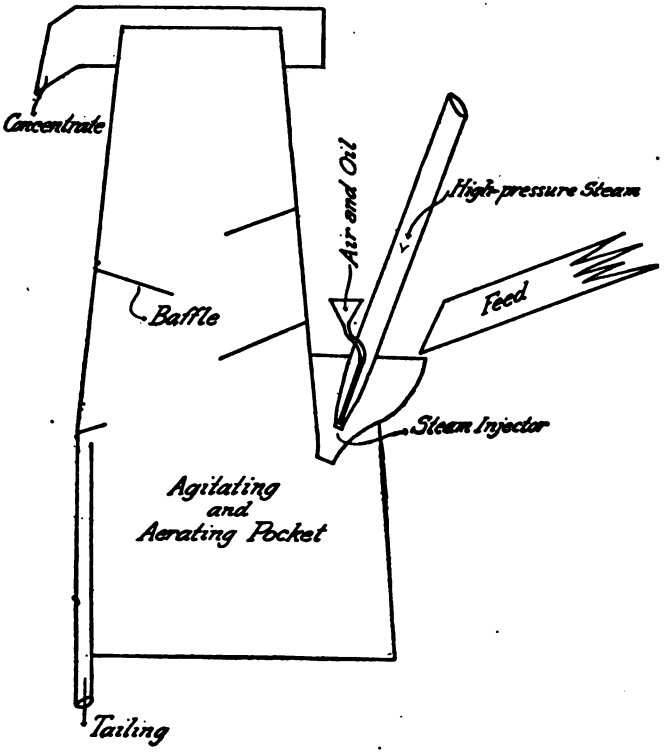


FIG. 5.

being led into the feed-hopper of the next. This type of machine is covered by the Ohrn patent.

The ideas covered by the Gröndal patent are similar to those embodied in the Ohrn apparatus, except that the oil is forced into the steam-pipe, and the mixed steam and oil then pass to a Koerting steam-jet apparatus where air is drawn in. The steam, oil, and air become thoroughly commingled, and the mixture is

led to the bottom of the agitating-compartment, which it enters through a funnel-shaped orifice. Unlike the Ohrn machine the pulp is fed direct into the agitating-compartment over the mouth of the funnel.. After violent agitation in one chamber, resulting from the entry of the steam-oil-air mixture, the pulp passes to another, where the froth and tailing separate and are removed. The method of feeding the pulp direct into the agitating-compartment, instead of through the injector, seems to be preferable, except in the case of the multiple treatment above mentioned.

The various machines that have been devised to take advantage of the Cascade principle have been touched upon in the briefest manner, to indicate the lines along which development has proceeded. Many modifications and elaborations will suggest themselves, to suit local conditions, and a wide field for experiment and research lies open to produce a machine possessing a maximum of the strong points of the Cascade process, with a minimum of mechanical complication.

Hitherto, in air-froth flotation practice, metallurgical and mechanical efficiency have followed somewhat divergent paths, but perhaps a by-way, connecting the two, will be suggested by the process as outlined in the preceding pages.

FLOTATION OF SEMI-OXIDIZED SILVER ORE[1]

By E. J. Atckison

About a year ago a pronounced effort was made to adapt the process of flotation to Mexican silver ores.[2] This was caused by the high price of cyanide. Since cyanide can now be obtained at a more moderate figure the new process has become less inviting. Few of the companies met with much success. The Santa Gertrudis, Real del Monte, and Amparo companies have no doubt done the most work on flotation. According to the report of the Department of Mines of Mexico the extraction at both the Real del Monte and the Santa Gertrudis was about 50% of the total gold and silver, but I was informed later by representatives of these two companies that an extraction of about 85% was expected after making a few minor changes in the flow-sheets.

The Amparo Mining Co., at Etzatlan, Mexico, in the preliminary work used one K & K machine (type 2612) as a "rougher," and a Callow cell as a "cleaner." The Callow cell was constructed of wood by Mexican carpenters, while the K & K was a factory-made machine. A battery of 10 stamps crushed the ore to 20-mesh. The pulp then passed to a Dorr classifier, the overflow going to the K & K, and the coarse product to a Krupp tube-mill. The tube-mill discharge was returned to the classifier, so that the feed to the flotation-mill consisted of 90% minus 150-mesh material.

Sodium sulphide at the rate of one kilogram per ton was used for sulphidizing. A number of different oils and oil-mixtures was tried; G. N. S. No. 5 and G. N. S. No. 22 gave the best

[1] From the *Mining and Scientific Press* of April 27, 1918.

[2] This work was performed under the supervision of J. H. Howard, general manager, and William Howard, assistant general manager for the Amparo Mining Company.

recovery. The practice was to add the sodium sulphide and the collecting-oil direct to the tube-mill, and the pine-oil to the classifier overflow. A rough concentrate was taken from the K & K machine and re-cleaned in the Callow cell. The rough concentrate averaged three kilograms of silver per ton. The tailing from the K & K was sent to two settling-tanks, where a small amount of lime was added, the clear water being pumped back to the battery. The pulp varied between 8 and 15% solid. On account of the water necessary in the battery it was impossible to keep a dense pulp without thickening. In this test 748 metric tons of ore was treated, giving an average recovery of 72% of the silver and 85% of the gold. The heading assayed 376 gm. silver and 8 gm. gold. Cyaniding the flotation tailing was tried, and it gave an extraction of about 50% of the silver, or a total of 86% of the silver and over 90% of the gold. This was about equal to the results obtained in the cyanide plant at that time, but it took as much cyanide to extract the 50 odd grams of silver in the flotation tailing as it did to extract 320 gm. of silver in the cyanide plant. It was also noticed that the solution fouled quickly when treating the oily tailing.

The concentrate from the Callow cell averaged 15 kg. silver, 380 gm. gold, 16% lead, 9% zinc, 5% manganese, 20% iron, 4% lime, and 16% silica. A great deal of difficulty was experienced in handling the concentrate. No filter was available, but the concentrate was settled in the four "pilas" (3 by 4 by 7 ft.). When a "pila" showed concentrate within four inches of the top, the flow was diverted from it, the concentrate was allowed to settle for a few hours, and then sacked.

Following this test an effort was made to thicken the pulp in a Dorr thickener before flotation. The pine-oil was added direct to the K & K machine, but the flow-sheet otherwise remained the same as in the previous test. So as to be able to get a thickened pulp, 8 kg. of lime per ton of ore was added in the battery-bin. The result was disastrous. A voluminous froth that carried a very small amount of concentrate appeared on the flotation machines.

The concentrate coming from the cleaner-cells assayed only

about 3 kg. of silver, the recovery being 50% of the silver and 55% of the gold. The lime was poorly burnt, thus accounting for the amount used. As soon as the addition of lime was stopped the machines started to produce the proper froth. An analysis of the lime was made to see if the cause of the trouble could be detected. As stated before, previous to this time it was the custom to add lime to the flotation tailing for settlement and pump back the clear water. The return-water carried about 0.25 kg. of lime (CaO) per ton, and for 12 hours each day only the return-water was used in the battery.

	Analyses of Lime	
	%	%
SiO_2	29.5	29.6
Fe_2O_3	5.4	10.7
Al_2O_3	3.5	3.2
CaO	41.3	38.5
MgO	1.8	1.5
Mn	less than 1%	
CO_2	considerable	amount

The froth produced at this time reminded me of that obtained when experimenting with some lead-carbonate ores. These apparently sulphidized nicely, but a recovery of about 50% was all that could be obtained. In almost every case where the recovery was low a voluminous froth appeared. The conclusions reached after the first series of tests were that:

1. Sulphidizing was indispensable with the oxidized ores.
2. Fine grinding was essential to free the mineral.
3. Two machines in series were necessary, in order to increase the recovery.
4. The density of the pulp must be 4 or 5 : 1.
5. Raw lime added ahead of flotation was detrimental, but enough lime to promote settling could be obtained by adding it to the flotation-tailing and then pumping back the clear overflow.

While waiting to install another K & K machine and rearrange the flow-sheet a series of experiments was made in a

EXPERIMENTS IN A JANNEY MACHINE

Test No.	Heading		G. N. S. No. 5, gm. per metric ton	G. N. S. No. 22, gm. per metric ton	Na_2S gm. per metric ton	Gasoline gm. per metric ton	Recovery		Remarks.
	Silver, gm.	Gold, gm.					Silver, %.	Gold, %.	
1.....	424	8	100	200	...	...	41	75	1 litre SO_2 added
2.....	424	8	50	100	...	...	59	76	36 kg. H_2SO_4 per ton
3.....	424	8	100	100	400	...	30	30	2 litres SO_2 solution
4.....	424	8	100	100	400	...	83	93	36 kg. H_2SO_4 per ton
5.....	424	8	100	200	1000	...	80	87	
6.....	424	8	100	200	400	400	84	94	
7.....	413	7	50	50	500	500	84	92	
8.....	210	3	50	200	500	400	85	90	Slime, −200 mesh
9.....	300	8	50	200	500	400	75	87	Sand, −100 mesh
10.....	255	5	100	200	500	400	85	96	
11.....	255	5	100	200	500	...	78	90	
12.....	240	4	50	200	...	400	75	87	1 kg. NaOH per ton
13.....	376	6	100	200	500	400	75	90	Na_2S and gasoline added after the oil
14.....	340	8	100	...	500	...	87	90	½ kg. Calif. crude oil per ton

Janney testing machine. It was found early in the work that a good extraction could be obtained by adding sulphuric acid to the pulp. However, the amount required, namely, 40 kg. per ton, was prohibitive. Gasoline was tried, and was found to be as good a flotative assistant in this case as acid. How the gasoline works is doubtful. The idea was that the gasoline cleaned the oxidized mineral and allowed the sodium sulphide to act upon it.

Assuming this to be the case, gasoline was added to the pulp in the proportion of 4 : 1 first and was then agitated two minutes in the Janney machine before adding the sulphide of sodium and the oil. Too much emphasis cannot be placed on the use of gasoline in flotation. With lead, zinc, and copper, and with graphite, the results in most cases were as good as when acid was added.

One thing is noticeable in these, as well as in all the other tests, namely, that the gold floats more readily than the silver. These experiments were conducted under as nearly the same conditions as possible and each experiment represents the average of three parallel tests.

The final test was divided into two periods. During period A 310 tons was treated, and during period B 204 tons. The flow-sheet is shown in the accompanying diagram. While treating the last 514 tons more oxidized ore than usual was drawn from the upper levels of the mine. This was much better from an experimental point of view, for the sulphides float readily. The Wilfley table acted as a pilot.

PERIOD A

	Heading, gm.	Tailing, gm.	Recovery, %
Silver	334	53	84.1
Gold	5.6	0.6	89.3
Total	...	...	85.9

Oil used: G. N. S., No. 5, 0.1 kg. per ton, plus G. N. S., No. 22, 0.3 kg. per ton.
Sodium sulphide: 0.8 kg. per ton.
Pulp: dilution, 18% solid; fineness, 90%—200 mesh.
Assay of concentrate: silver, 12.035 kg.; gold, 240 gm.
Wilfley table concentrate: 926 kg., assaying silver 776 gm. per ton; gold 14 gm. per ton.
Tonnage: 40 tons per 24 hours.

During period A the entire load was thrown on one K & K machine for three days. This brought the recovery down somewhat. The froth from the No. 1 K & K machine assayed about 6 kg. of silver per ton, while the froth from No. 2 was a trifle over one kilogram.

PERIOD B

	Heading, gm.	Tailing, gm.	Recovery, %
Silver	320	44	86.2
Gold	6	0.5	91.6
Total	...	...	88.1

Oil used: G. N. S., No. 5, 0.1 kg. per ton; G. N. S., No. 22, 0.25 kg.
Sodium sulphide: 0.75 kg. per ton.
Pulp: same as in test A.
Assay of concentrate: silver, 12.671 kg.; gold, 232 gm.
Wilfley table concentrate: 806 kg., assaying silver 859 gm. per ton; gold 18 gm. per ton.

Cost of Flotation *v.* Cyanidation.—To simplify the calculations, let us consider the recovery the same by flotation as by cyanidation, although the extraction by cyanide is a trifle better. The cost of freight and treatment on one ton of concentrate is $19.22. From this would be deducted the premium on the lead, which would be about $5. The cyanide plant now produces one ton of concentrate per 24 hours from the sand and slime tables. A 300-ton all-flotation plant would have an output of about 7 tons of concentrate per 24 hours. Flotation costs in the mill would amount to 95c. per ton, which includes the cost of fine grinding, chemicals, labor, water, repairs, and minor items. Another charge of $2.46 per ton covers the cost of marketing the concentrate, taxes, and a loss of 5% of the silver and gold, as the smelter pays for only 95% of the assay-value. This makes a total cost of $3.41 per ton.

Cyanidation, when the value of cyanide at the works is 75c. per kilogram (34.1c. per lb.), costs $3.92 per ton, which includes the cost of marketing the bullion and other expenses. This leaves 51c. per ton in favor of flotation. Cyanide at a

normal price of 35c. per kg., with an extraction 1% higher by cyanidation, would more than make up the difference. There

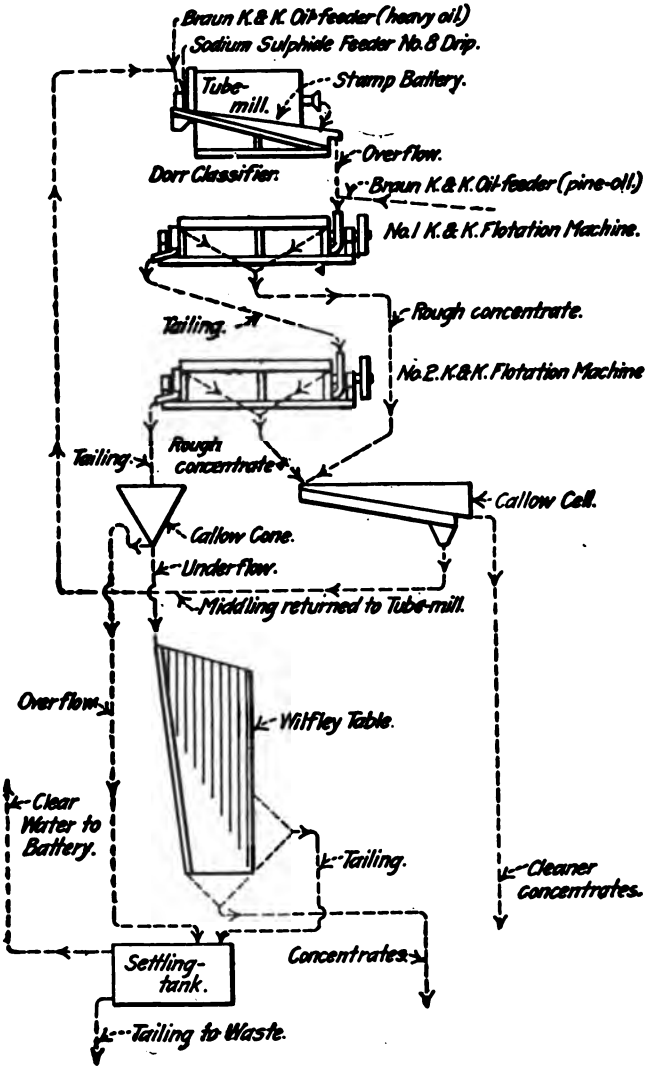


FIG. 1.—Flow-Sheet for Flotation of Semi-Oxidized Silver Ore.

is also the interest and depreciation on the flotation plant to deduct. To make the change from the present plant to an all-

flotation mill would cost about $40,000, including the necessary re-grinding machinery.

The success of flotation seems to be determined by the treatment of the concentrate. If a supply of Mexican crude oil could be obtained at a reasonable figure, it would be a simple matter to install a small roasting-furnace, and, after roasting the concentrate, to melt it in a reverberatory furnace. The base lead bullion could then be cupelled, producing fine gold and silver bullion and litharge. A market for the litharge would have to be found. The consumption of cyanide on the raw ore amounts to three or four times the silver content. If the heading averages 300 gm. silver the cyanide would amount to about one kilogram per ton. This ratio of cyanide to silver holds true in the flotation concentrate. The experiments showed that a 12-kg. concentrate would require about 45 kg. cyanide. It was noticed in cyaniding the concentrate that the gold went into solution much more readily than the silver. The heavy collecting oils retard the cyanidation materially. A gasoline wash before cyaniding is quite effective. Since it required practically the same amount of cyanide to treat the flotation concentrate as it did to cyanide the ore, the question of cyaniding the flotation concentrate puts one where he was in the beginning as regards the cyanide.

TESTS SHOWING EFFECT OF OIL

Oil	NaCN 98%, gm.	Time, hr.	Mesh	Recovery	
				Silver, %	Gold, %
None	0.2	70	−100	84	90
Pine-oil	0.2	"	"	79	85
Pine-tar	0.2	"	"	76	84
Coal-tar	0.2	"	"	72	82
Crude oil	0.2	"	"	66	69
Creosote	0.2	"	"	78	75
Pine-oil	0.2	118	"	87	92
Pine-oil	0.3	70	−150	87	89
Pine-tar	0.3	72	−200	86	87

The heading assayed silver 326 gm. and gold 7 gm. In all of the experiments 100 gm. of ore was taken, 300 c.c. of water, and a small amount of CaO. The oil used was equivalent to one kilogram per ton. The cyanide consumption was practically the same in all the tests. The ore, oil, and water were mixed for five minutes in the Janney testing-machine before the cyanide was added.

THE DEVELOPMENT OF FLOTATION AT THE BROKEN HILL PROPRIETARY MINE, AUSTRALIA[1]

By Edwin T. Henderson

Toward the end of 1902, with a view to finding a means of obtaining a zinc concentrate from the dump-tailing, the late A. D. Carmichael, the company's research chemist at that time, was instructed by G. D. Delprat, general manager for the Broken Hill Proprietary Co., Ltd., to carry out some experiments with nitre-cake (sodium-sulphate) of which we had a large stock. It was observed on placing some of the tailing in a strong solution of this salt in a beaker and heating it, that the sulphides were floated as a high-grade concentrate leaving the gangue in the bottom of the beaker.

An experimental plant was immediately started, and the results obtained were so encouraging that patents were applied for in November, 1902, it being believed that this was something absolutely new in concentration methods.

Considerable difficulty was experienced at first in placing this new process on a commercial footing. First one type of separation vessel was tried and then another, until about a dozen had been used before a suitable one was designed. However, by the beginning of May, 1903, fifty tons of zinc concentrate had been produced by the process from tailing that was ordinarily dumped. This parcel was the first 50-ton lot of zinc concentrate ever produced by flotation. After this the process made rapid strides, and by October, 1904, was treating 500 tons of feed daily, which amount was gradually increased until, by October, 1905, the output exceeded 1000 tons per day.

For the first four years this Delprat process was the subject

[1] From the *Mining and Scientific Presss* of September 21, 1918.

of considerable litigation, the cause of which was a prior patent taken out by the late C. V. Potter, in November, 1901, for obtaining the same result by the use of dilute acid solutions. Potter's patent was wide in its claims, vague, and in several parts erroneous, and it was contended that his patent was invalid, this contention being upheld by the Courts through which it passed. It was finally sent to the High Court, but prior to coming before that tribunal an agreement was reached between the parties concerned by which the Broken Hill Proprietary Co. obtained the free use of either the Delprat or the Potter patents.

From this time onward, owing to sulphuric acid being substituted for nitre-cake in the solution, the method became known as the Delprat-Potter process. It has been free from litigation, but the patents have now expired.

Although this process has been the subject of previous papers, there still seems to be some doubt in the minds of certain writers concerning some of the details, so that a brief outline of our practice at Broken Hill may be of value.

The feed consists of various tailings produced in the gravity-concentration mills, either from crude ore or old dumps, by crushing, jigging, and tabling for the removal of the lead, and classification for the removal of the slime. It is delivered to the bins of the flotation plant by a series of belt-conveyors.

This feed assays from 13 to 15% zinc, from 3 to 3.5% lead, and from 5 to 6 oz. silver per ton. An average sizing-test shows:

	%
On 40	7.0
" 50	6.5
" 60	10.5
Through 60	76.0

The gangue in the feed consists mainly of rhodonite, garnet, and quartz, with small amounts of fluorspar, calcite, and siderite. The feed as delivered to the plant carries from 9 to 11% moisture.

The feed-bin has a capacity of 170 tons. The conveyor is set on top of this bin, and the feed can be dumped at any desired point. The discharge from the bin is by means of twin

Archimedean screws set in the bottom of the bin opposite each separating-vessel. The amount discharged is regulated by slide-doors, which on being lowered partly cover the forward ends of the screws.

The cast-iron separating-vessels, of which there are five, are of the shape shown in Fig. 1. They are 9 ft. square at the top, 2 ft. by 1 ft. at the bottom, and 15 ft. deep. The feed from the screw-feeders is delivered behind the baffle *A*, which dips a few

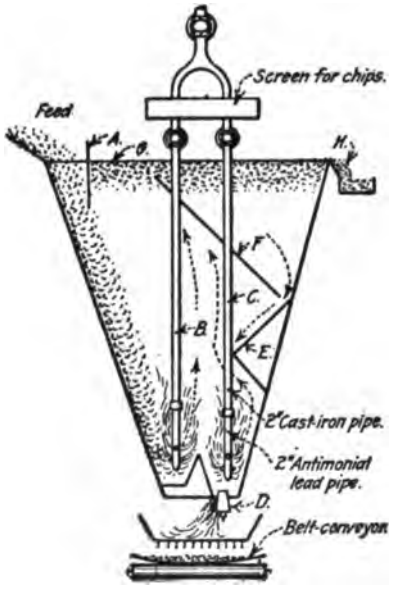


FIG. 1.

inches below the level of the solution. It then slides down the back until it reaches the solution-jets at the bottom of the pipe *B*. These jets deliver the solution at a pressure of approximately 15 lb. per sq. in., at a temperature of 200° F. and an acidity of 1% H_2SO_4. The object of these jets is to keep the feed in suspension while the acid acts on the carbonates in the feed, liberating CO_2. This gas attaches itself to the sulphides and floats them to the surface. The back-jet *B* washes the feed to the front of the vessel where it meets another jet *C*, which gives it the final treatment. Any stones or other foreign matter in the feed lodge

in the pocket below the jet *B* and accumulate there until such time as the vessel is emptied, when they are removed.

The tailing, after treatment by the jet *C*, passes through a hole in the plug at *D* in a practically continuous stream. The up-current in the separating-vessel, together with the stream of sulphides floating to the surface, tends to carry up some of the lighter gangue. In order to give this a chance to separate, two baffles are placed in the vessel. The one shown at *E* deflects the rising sulphide from the front and causes it to come into contact with the baffle *F*. It then moves up the under side of this and is delivered at the surface at the point *G*. It then floats toward the overflow at *H* on comparatively still water, and most of the gangue that was carried up falls again on to the top of the baffle *F*, down which it slides and falls to the bottom of the vessel.

The concentrate overflowing at *H* passes in a launder to a settler, where most of the accompanying solution is separated. The solids, together with a small amount of liquid, pass through plug-holes in the bottom of the settler on to a belt-conveyor, where the solution is drained and the concentrate removed to the bin. The tailing delivered at *D* falls into a trough with a perforated bottom, which breaks the fall, and then to a belt-conveyor where the solution drains and the tailing is delivered to a series of conveyors, which takes it to the dump.

The solution separated from the concentrate and tailing contains a small amount of slime, and to remove this it is passed over settlers. It is then pumped to the elevated solution-tanks, which give it the necessary head, by the Harris system of pumping by means of compressed air. This is done in two stages, the first lift being about 40 ft. and the second about 30 ft. Between these two lifts the solution passes through another settler, to remove any remaining slime, and then to a box feeding the second lift. To this box sufficient acid is added to bring the solution back to approximately 1.0% H_2SO_4. Air-jets are used as a stand-by in case anything happens to the Harris pumps.

The fall in temperature of the solution is about 25° F. It varies slightly, depending on the temperature of the atmosphere and the feed treated. The consumption of acid is about 26 lb.

per ton of feed treated. Approximately 30,000 gallons of solution is circulated per hour in the plant when running full and treating 80 to 85 tons per hour. The temperature of the solution in the elevated tanks is kept between 200° and 212° F. by blowing in superheated steam from the B. & W. boilers.

All the solution-pipes and the separating-vessels are made of cast-iron. On first being used they are slightly corroded by the hot acid solution, but they soon become coated with a thin layer of graphite from the iron, and this protects them from further corrosion. The separating-vessels and the return-solution pipes become coated inside with a layer of gypsum, which gradually grows in thickness and has to be removed occasionally. This deposit of gypsum is greatest wherever the solution is subject to a sudden fall in temperature, for example, where the air enters an air-jet.

Each separating-vessel treats from 15 to 20 tons of feed per hour. They require very little attention, and the whole plant is as nearly fool-proof as anything can be. The life of the separating-vessels is practically unlimited, provided the bottom portion is protected from abrasion by inserting a lining of wood.

Only 12 men and 2 boys are employed in the plant to treat 550 tons per shift of eight hours. The repairs are light, as there are few moving parts that come in contact with the feed or solution. The cast-iron screws on the feeders are made so that they can easily be replaced. The jets in the bottom of the separating-vessels are made of antimonial lead, and are burnt onto a 2-in. lead pipe; this pipe is about 18 in. long, and is flanged at the top and bolted to the cast-iron pipe. These can be easily removed when the holes become too large by replacing them with spares, the old ones being sent for repair.

The plugs that let the tailing out are made of antimonial lead; they are cast in a mold and are quickly and cheaply made. These plugs can be lowered by means of the lever-gear to which they are attached and enable any foreign substance to be discharged through the 4-in. diam. plug-hole. The hole in the plug itself for the discharge of the tailing is made about $\frac{3}{4}$ in. diameter. The worn plugs are melted, a small amount of fresh metal being added

to make up for the wear. It is then re-cast. The plugs can be easily changed while the pan is in operation. A lever with a forked end is placed under the shoulder of the plug to be removed to hold it in position; the spindle that supports the plug is then lowered and a new plug placed on it. The forked lever is then withdrawn, so as to allow the old plug to fall, the new plug being raised into its position. The wear on the hole through these plugs is largely taken up by inserting iron rods of varying thickness, according to the amount of wear, and they are only changed when the hole becomes too large for this treatment.

That portion of the separating-vessel that comes under the action of the solution-jets is lined with wood to prevent the sand scouring the cast-iron sides. This wood is renewed when it wears. The plug-seats are cast of antimonial lead, but these do not require to be renewed often, as the plugs fit well into them, and there is practically no leakage between the seat and the plug.

The concentrate produced by this treatment averages as follows: zinc, 47%; lead, 6%; silver, 13 oz. per ton. An average sizing test shows:

	%
On 40	7.7
" 60	15.1
" 80	21.5
" 100	13.5
" 150	14.1
" 200	11.1
Through 200	17.0

The tailing assays 3% zinc, 2% lead, and 2 oz. silver per ton.

Some doubt has been expressed as to whether oil is used in this treatment or not, and I wish to make it perfectly clear that oil is not used in any shape or form in this process. It has been suggested that oil was introduced into the solution by using exhaust-steam from engines to heat the liquor, but since nothing but live steam from the B. & W. boilers is used, this is obviously not the case. It has also been said that the ore in passing through the milling operations picks up oil used for lubricating, and also that while being mined it is splashed with oil from the rock-drills; some even suggest that the ore naturally contains oil. No doubt

some oil does come in contact with the ore in the milling operations, and also underground, but the amount is infinitesimally small, and although the concentrate produced has been tested on several occasions no trace of oil has been detected.

To show that the float is made without any oil, some ore was crushed and heated at a temperature of 400° C. for one hour, which should destroy any oil present. It was then treated with a 1% H_2SO_4 solution made up with distilled water and strong acid. A good float resulted.

This process is not adapted for the treatment of slime. The feed contains approximately 2 to 3% of slime, but if this amount is increased appreciably a low-grade concentrate is the result. The slime is also high in lead, and if included in the feed to this process it would raise the lead content of the concentrate produced. For the above reasons, the slime is separated as thoroughly as practicable from the sand in the milling operations, and only the sand sent to this plant. For some years the slime was run to dams and stored, awaiting a suitable treatment.

In 1910, Leslie Bradford discovered that by agitating this slime with a heated acid solution in a centrifugal pump, delivering into a separating-vessel, the sulphides would float as a high-grade mixed lead and zinc concentrate, without the use of oil. A plant was erected capable of treating 3000 tons of slime per week. This was run for several months, and produced several thousand tons of concentrate assaying zinc, 34%; lead, 25%; and silver, 40 oz. per ton. The tailing assayed zinc, 4%; oxidized lead, 8%; total lead, 9%, and silver, 4 oz. per ton.

This concentrate was roasted and sent as feed to the zinc-retorts at Port Pirie, but the quantity produced was largely in excess of the amount required for this purpose, and the plant was closed down until such time as the supply of concentrate was used up, or until a more favorable market became available.

The temperature required for this treatment was 140° F., and the acidity of the pulp was about 0.3% H_2SO_4. The separation was complete with four agitators and separating-vessels placed in series. The acid was added partly to the pulp at the

head and partly to the suction of the various agitators. These agitators and separating-vessels will not be described here, as they are the same as those used in our present treatment, which will be described later.

The difficulty of marketing these mixed lead-zinc concentrates spurred the officers of the metallurgical department to find a better way of treating the slime, so as to get a zinc concentrate practically free of lead and a lead concentrate practically free of zinc. That the galena was much more readily oxidized than the blende was well known. In fact, the high lead content of the tailing produced by floating the sulphides from the slime was due to the oxidation of the galena during milling and subsequent exposure on the dumps.

In 1908, E. J. Horwood proposed that this property of lead sulphide be utilized in separating lead and zinc sulphides in slime, and in this connection a considerable amount of experimental work was done by the metallurgical staff, with the object of finding a commercial method of bringing about this oxidation. These experiments were finally successful, and led to the patenting in October, 1908, of the Horwood process, the pioneer selective flotation process. This process is for the recovery of blende by flotation from ores containing blende, galena, and (or) pyrite. This is accomplished as indicated above, by oxidizing the galena and (or) pyrite and so rendering them unamenable to flotation while the blende, not being attacked, is floatable.

The most suitable way of bringing about this oxidation was found to be by roasting the slime or the mixed concentrate at a temperature of 400° C. and rabbling freely with a plentiful supply of air. If the ore to be treated contains soluble salts these should be removed by washing, as otherwise they will cause the blende to be attacked; this will cause loss of zinc, owing to solution and high acid consumption.

Oxidizing the lead in the wet way was also patented by Mr. Horwood, but when oxidizing agents are used the zinc is invariably attacked, although, of course, not to the same extent as the lead. The more rapid the action of these reagents on the galena, the greater the amount of blende dissolved, and only by making

the oxidizing solutions weak is this trouble overcome, but then the time required to sulphatize the lead becomes excessive.

It was found that, with Broken Hill and like ores, the best temperature at which to sulphatize was 400° C. At this temperature the galena sulphatizes rapidly, while the blende is not affected. In the case of ores other than those of Broken Hill, carrying a large amount of pyrite, as well as zinc and lead sulphides, the temperature can nearly always be safely carried to 500° C., especially while the pyrite is burning. Little or no lead sulphate will be formed while pyrite is present, so this is burnt off rapidly.

Ores containing resinous blende invariably stand a higher temperature than those in which the blende is ferruginous. The sulphating operation requires plenty of air, and a good draught over the ore in the furnace is essential. While the sulphur is being burnt from the pyrite, the ore will tend to flow somewhat, but as soon as the galena starts to oxidize the particles seem to cling together, and very little dusting occurs.

The extent to which the sulphating has to be carried to prevent the lead from floating varies with different ores. In some cases a 10% sulphatization is sufficient, while in others as much as 60 or 70% is required.

The subsequent flotation of the blende in the roasted ore is a simple matter, provided, of course, the temperature has been kept within the limit mentioned, and the soluble salt content of the ore treated was low. A slightly acidulated solution at a temperature of 130° F. has nearly always been found to give the best results.[2]

If no oil is used, the solution should be high in soluble salts, and should carry from 1 to 3% of sodium sulphate. The sodium sulphate acts as a mineral-frothing agent, and its use was covered by Patent No. 10640/13 in the Commonwealth of Australia by Mr. Bradford. A large number of tests have been made on a great variety of ores, and the process has been proved to have a wide application. In order to make tests on a working-scale, a

[2]Details of this process appeared in the Transactions of the Australian Institute of Mining Engineers, Vol. 16, for 1912.

small flotation plant was provided by the Broken Hill Proprietary Co. at the Bendigo School of Mines, where the requisite roasting-plant was already available. Working-tests were carried out to demonstrate the practicability of the process on both Broken Hill slimes and Tasmanian complex sulphides, from which latter a zinc concentrate assaying over 58% lead was obtained.

Owing to the litigation between the rival claimants to the oil-flotation processes, which were then considered necessary for slime-flotation, the Horwood process was not used at the Proprietary mine, but was adopted by the Zinc Corporation, on whose property a plant to treat 70 tons per day of a mixed lead-zinc slime concentrate was erected. The plant was working for about 12 months, but operations were suspended on the outbreak of war, as there was no sale for the concentrate produced.

The roasting was carried out in an Edwards duplex furnace of 12 panels, and this was found to answer well for the sulphatizing operation. The float was produced in a Minerals Separation machine of the staggered type, using eucalyptus oil as the frothing-agent.[3]

By the time litigation between the oil-flotation claimants ceased in Australia, Mr. Bradford and I, working together, had obtained encouraging results experimentally in preferential flotation without roasting, indicating the advisability of awaiting further developments before installing any selective process for the treatment of slime.

Before proceeding to describe the other methods of preferential flotation developed at our mine, a short account of the theory of flotation, as held by those engaged on the work, may prove useful to the reader. The old theory that flotation was due to the aversion of the sulphide particles to becoming wetted and that they were always surrounded under normal conditions with a film of air, is the one generally accepted here. Whether this aversion on the part of the sulphides is caused by electric charges, as first advanced by Professor Huntington in his evidence before the Royal Commission on the Potter-Delprat process in 1904, or not, has never been determined, for, in fact, it has always been

[3] A full description of this plant and its application is to be found in the Proceedings of the Australian Institute of Mining Engineers, No. 12, of 1913.

looked upon as a natural property of sulphides. From a purely scientific point of view, it would undoubtedly be interesting to know why sulphides have this property, but from a practical point of view the fact that they have this property is self-sufficient. For the average man running a flotation plant, the simpler the theory the better. It is no good going to such depths that he cannot grasp the meaning, for then instead of being a help the theory only confuses him.

From the above old theory two main ideas attracted those who were engaged in experimental work on preferential flotation: (1) Since all sulphides have an aversion to becoming wetted, whereas oxidized minerals have not, or have not in the same degree, then a separation of one kind of sulphide from another kind of sulphide might be brought about by changing one of them to an oxidized state. This was done by the Horwood process. (2) Since the sulphide particle floated by aid of the film of air that surrounds it, then by removing this film the particles will become wetted and will not float.

The problem of bringing about this removal of the film was solved by Mr. Bradford in 1912, and again in 1913. His first method was by treating the ore containing galena and blende with a slightly acidulated sodium-chloride solution. This solution, especially at a temperature of 140° F. and above, has a slight chemical action on the galena. This chemical reaction generates H_2S, which diffuses in the air films around the galena particles and gradually removes them. The rate at which the H_2S is generated gradually decreases as the solution becomes less acid, and finally reaches a point at which it is not generated as fast as it goes into solution. When this stage is reached, the galena is wetted by the solution coming into intimate contact with the surface of the particles. Now by agitating the ore in this solution, the blende will float, but the galena will not. The acidity of the brine solution must be low, otherwise the H_2S will be generated faster than it can go into solution, and in that case the galena will not be wetted and will float with the blende.

This is known as the Bradford salt-sulphuric process. It has never been worked on a large scale, because by the time it had been developed sufficiently to be put to commercial use, Mr.

Bradford had discovered another way of obtaining the results without the use of the brine solution.

The strength of the brine solution varies with the different ores under treatment, but from 5 to 10% NaCl will be found sufficient in most cases. The acidity must be kept low and should not exceed 0.03% H_2SO_4. A trace is nearly always sufficient. It is not always necessary to keep the solution acid throughout the separation. At the start it should be slightly acid, but this acidity will disappear before the separation has proceeded far, and it is then completed in the neutral solution. The temperature of the solution should be between 140° and 160° F.

Having removed the blende in this way, it may be necessary to concentrate the lead remaining in the residue before sending it to the smelter. This may be done in two ways: (1) By adding a small amount of a soluble copper salt to the brine solution, causing any sulphides remaining in the residue to float when submitted to aeration. (2) By removing the residue from the brine circuit and floating the lead in warm acidulated water.

The use of copper sulphate in assisting the flotation of sulphides was discovered by Mr. Bradford, and patented by him in 1913, Commonwealth Patent No. 8123/13. It was also covered for the same purpose by the Minerals Separation people in 1914, but Bradford's patent is recognized here in Australia. He did not cover its use outside the Commonwealth.

A practically complete separation of the lead and zinc sulphides can be made by the salt-sulphuric acid method giving a lead concentrate of 65% lead and a zinc concentrate of 50% zinc.

The following laboratory tests illustrate the capabilities of the process on Broken Hill crude ore:

No. 1.

	Weight, %	Zinc, %	Lead, %	Silver, oz.
Original	....	12.4	15.5	11.5
Zinc concentrate	20.9	50.6	3.5	11.2
Lead concentrate	18.6	6.4	69.8	39.5
Tailing	57.8	1.0	0.6	1.6

The distribution of metals is as follows.

	Weight, %	Zinc, %	Lead, %	Silver, oz.
In zinc concentrate	20.9	85.3	4.7	20.3
In lead concentrate	18.6	9.6	83.8	63.9
In tailing	57.8	4.6	2.2	8.0
		99.5	90.7	92.2

No. 2.

	Weight, %	Zinc, %	Lead, %	Silver, oz.
Original	....	15.8	16.0	12.9
Zinc concentrate	25.0	52.0	2.7	5.6
Lead concentrate	20.75	9.6	65.2	50.0
Tailing	52.5	1.2	2.7	1.6

The distribution of metals is as follows:

	Weight, %	Zinc, %	Lead, %	Silver, oz.
In zinc concentrate	25.0	82.3	4.2	10.8
In lead concentrate	20.75	12.6	84.5	80.8
In tailing	52.5	4.0	8.8	6.5
		98.9	97.5	97.7

The second method of removing the air-films from the sulphide particles was discovered by Mr. Bradford in 1913, and patented. This was brought about by either causing a soluble gas to be generated in the ore-pulp under treatment, or by forcing it in under pressure. The gas, by diffusing in the air-film surrounding the sulphides, causes the film to be removed, and then, being itself soluble, allows the solution to come into intimate contact with the surfaces, and so wets them. The soluble gas used is SO_2 and this is either generated in the pulp by adding hyposulphite (or any other reagent that will liberate SO_2) and

sulphuric acid, or by blowing SO_2 gas produced from roasting operations, or by burning sulphur into the pulp while it is being stirred. In some cases both these methods are used together. If the pulp, after being treated in this manner, is subjected to agitation with air, then those particles that have a greater aversion to being wetted will take the air and float, while those that have not such an aversion to being in this state will remain with the gangue.

This process has been in use on a large scale by the Broken Hill Proprietary Co. and also by the Broken Hill Junction North Co. for some time, and excellent results are being obtained. The process is now being adopted by several other Broken Hill companies, which have purchased the Broken Hill rights from Mr. Bradford. The complex sulphide ores from the Rosebery-Hercules mines, in Tasmania, containing blende, galena, and pyrite, gave a zinc concentrate containing up to 58% zinc, with recoveries from 80 to 85%.

The following laboratory test illustrates the work done by the process on Broken Hill slime:

	Weight, %	Zinc, %	Lead, %	Silver, oz.
Original	....	13.9	7.4	6.8
Lead concentrate	12.9	8.7	43.4	41.8
Zinc concentrate	21.4	50.7	4.0	3.4
Tailing	63.2	2.4	1.5	1.1

The distribution of metals is as follows:

	Weight, %	Zinc, %	Lead, %	Silver, oz.
In lead concentrate	12.9	8.1	75.6	79.3
In zinc concentrate	21.4	78.0	11.5	10.7
In tailing	63.2	10.9	12.8	10.2

A description of this process will form the subject of a separate paper.

THE BRADFORD PROCESS AT BROKEN HILL[1]

By Edwin T. Henderson

Since September 2, 1916, the Bradford process has been in operation on the Broken Hill Proprietary mine, Broken Hill, treating approximately 3000 tons of slime weekly.

The greater part of this slime is obtained from old slime-dams, the remainder being made up with current slime from the ore-dressing mills.

The dump material is loaded into trucks holding 1750 lb. each, and hauled to the plant by horses. Each train consists of four trucks, one horse being able to haul this quantity comfortably. Two horses are kept going constantly.

As the trains arrive at the plant they are tipped into a hopper placed below the ground-level. As each truck is tipped a boy throws a shovelful of nitre-cake weighing about 8 lb. into the hopper as an emulsifying agent, and this passes on with the slime. Recent tests indicate that the mineral salts in solution in the plant-water are themselves sufficient for emulsification. No oil is used for flotation purposes in this plant.

This hopper has a six-inch opening running the full length of the bottom, and delivers the slime as tipped onto a 24-in. belt-conveyor traveling at 260 ft. per minute. This conveyor carries and elevates the slime to a mixer 8 ft. diam. and 6 ft. deep, having an arm (6 ft. diam.) revolving at 42 revolutions per minute in the bottom. Solution is added here, and the slime is mixed to a flowing pulp.

The discharge from this mixer is taken from one side, 18 in. from the bottom. The pulp flows in a box-launder to a tube-mill loaded with flints and making 7 r.p.m. The purpose is to

[1] From the *Mining and Scientific Press* of September 28, 1918.

break up any small lumps of slime that have escaped the first mixer.

A screen, 32 in. diam. by 2½ ft. long, made of punched trommel-plate having ⅛-in. holes, is bolted to the discharge end of the tube-mill. This screen is fitted inside with an Archimedean screw, which revolves with the screen and works any wood-pulp or rubbish that will not pass the holes to the discharge, where it falls down a chute and is removed from time to time.

The pulp that passes through the screen flows in a launder to a storage-vat 30 ft. diam. by 5 ft. deep. This vat is fitted with revolving arms, 26 ft. diam., made of channel-iron, with scrapers attached similar to a Dorr thickener, only set to throw toward the periphery. These arms make 3 r.p.m. and keep the slime in suspension.

The current slime from the mill, after being de-watered in a Dorr thickener, is discharged to this storage-vat. The pulp in this vat contains 50% solid.

The vat is discharged by means of a 6-in. pipe bolted to the side close to the bottom. A gate-valve placed close to the vat regulates the flow. This pipe takes the pulp to an elevator that delivers to a small mixer at the head of the plant. This mixer is 5 by 5 by 5 ft. and has an arm 4 ft. 6 in. diam. revolving in the bottom at 29 r.p.m. Clear solution from storage-vats is added here in sufficient quantity to break the pulp down to 25% solid by weight.

Sufficient acid is added to acidify the pulp, and sodium hyposulphite to the extent of 1.5 to 2 lb. per ton. The latter is made up to a 30% solution on the ground-level and pumped to a 400-gal. tank placed alongside this mixer. The flow is regulated by means of a tap, which is adjusted to deliver one pint in 40 seconds. The flow through the plant ranges from 20 to 25 tons of solids per hour.

From this mixer the pulp passes through two short lengths of 6-in. pipe to a similar mixer placed on the same level alongside. The object of the mixer is to give the necessary time for the SO_2 liberated from the hyposulphite to wet the zinc sulphide.

The acidity, density, and temperature of the pulp are tested

in this mixer repeatedly. The best work is obtained when the acidity is between 0.025 and 0.03, the temperature between 85 and 90° F., and the density between 23 and 26% solid by weight.

The density is obtained by filling a bottle made of tin and calibrated to hold 1000 c.c. H_2O at 90° F. The density of the circuit-liquor runs at 1.05 sp. gr., and a table is fixed alongside the balance showing the percentage of solid corresponding to any weight of charge.

The discharge from this second mixer is through a 4-in. cast-iron pipe bolted to the side of the mixer, and about 6 in. above the bottom. A slide-valve is placed over the mouth of this pipe in the mixer, and this is adjusted by means of a screw, to give any desired flow. The pipe delivers to the suction of the first agitator of the lead section.

These agitators are of a special design. They are in the form of a centrifugal pump and act in the same way, but give a much better agitation. The runner consists of a circular disc on the sides of which two rings of pegs project a distance of $1\frac{1}{2}$ in. from the face; the runner is $17\frac{3}{4}$ in. diam. Lining plates are placed inside the casing of the agitator. The side plates have two rings of pegs similar to those on the runner. One of these rings fits between the two rings on the runner, and the other between the smaller ring and the centre. The suction-pipe is coupled to both sides of the casing, so that the pull on either side of the runner is balanced. A half-inch pipe is tapped into the suction on both sides of the casing, and these are joined up on top to an inch pipe, which is in turn coupled to a 3-in. main running along the top of the plant. This main is connected to sulphur-burners, to be described later. Through these pipes the agitators draw their supply of air and sulphur di-oxide.

The runner in the agitator revolves at 1080 r.p.m. The gas and pulp entering at the centre have to run the gauntlet through the revolving and stationary pegs on the runner and side plates, and the air is thoroughly broken up. Clear solution at a suitable pressure is delivered through half-inch pipes near each gland to prevent the grit coming into contact with the gland, and thus reduce the wear on spindles.

The agitator delivers through a 4-in. pipe into a separation-box (see Fig. 1) where the lead sulphide floats and forms a froth 3 ft. deep, overflowing on top so as to pass to the main lead-concentrate launder.

From one side near the bottom of each separation-box a 4-in. cast-iron pipe leads to the suction of the next agitator of the series. A slide-valve fitted inside each box, and operated by an iron rod passing to the top of the box, controls the flow from one box to the next. The control of the flow of pulp through the agitator also regulates the amount of gas drawn in and incidentally the

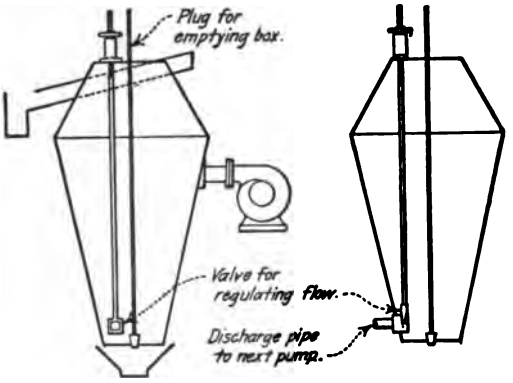


FIG. 1.—Sketch of Separation-Box

power consumed. The smaller the flow the greater the supply of gas and the smaller the power required, and the reverse.

There are nine of these agitators in the series, each drawing dilute SO_2 from the burners and delivering the agitated pulp to a separation-box where the lead floats off. Most of the lead is removed in the first four boxes, and after this the lead on each succeeding box becomes shallower, until at the ninth practically nothing remains, and it is allowed to overflow slightly. This overflow is returned to the head of the system.

It is found that the lead is cleaner if a small amount of acid is added to boxes No. 6 and 7; the solution has become neutral by this time, and the addition should be just sufficient to make it slightly acid. Steam is also added to the last four agitators to raise the temperature in No. 9 box to 90° F.

The agitators are driven in pairs by means of a belt from the main shaft, which in turn is belt-driven from a 250-hp. engine.

The discharge from No. 9 separation-box is through a 4-in. cast-iron pipe, fitted with a valve to control the flow. This pipe delivers the pulp to two 30-ft. Dorr thickeners, 10 ft. deep, which settle the zinc middling and give clear solution at a temperature of about 90° F. flowing to the solution-tanks at the head of the lead section.

The lead concentrate overflowing from these separation-boxes passes in a common launder to a storage-vat placed on the ground-level. This vat is 20 ft. diam. by 5 ft. deep, and is fitted with stirring-arms making 14 r.p.m., so as to keep the solid in suspension. The pulp in this vat contains 40% solid by weight, subsequently thickened in a storage-vat, 14 ft. diam. by 18 ft. deep, to 70% solid, whence it is pumped by means of a three-throw plunger-pump to filter-presses of the Dehne type; each press has 50 leaves, and the cakes are 3 in. thick.

The press holds 9 tons of lead concentrate. Two of them are required to press and dry the concentrate produced. The drying is done by blowing compressed air at 80 lb. pressure through the cakes for 30 minutes. The moisture is in this way lowered to 10%. The cakes, when dropped from the press, fall onto bars placed over a conveyor; this delivers its load to a second conveyor, which carries it to the bins.

The arms on the Dorr thickeners treating zinc middling make one revolution in 1½ minutes. The discharge from these, containing 60% solid by weight, is delivered to an elevator that lifts to an overhead launder running to two vats, 20 ft. diam. and 7 ft. deep, which act as storage-vats for the zinc section. These vats are fitted with revolving arms making 14 r.p.m., to keep the solid in suspension. Steam is blown into the pulp in these vats, and the temperature is thus raised to 125° F.

An elevator is placed between these two vats and they discharge to it, through 4-in. cast-iron pipes fitted with a valve to regulate the flow. These pipes are bolted to the sides of the vats and are about 2 ft. long. This elevator raises the pulp to a launder delivering to a small mixer 5 by 5 by 5 ft. at the head of

the zinc section. This mixer has an arm 4 ft. 6 in. long revolving at the rate of 29 r.p.m. Here solution from the zinc-section solution-tanks is added to break down the pulp to about 20% solid, and acid equal to 30 lb. per ton, to acidify the pulp to approximately 0.3%. The temperature of the pulp is about 125° F.

The discharge is through a 4-in. cast-iron pipe, fitted with a slide-valve in the mixer similar to the lead section. This discharge-pipe connects to the suction of the first agitator, which has a half-inch pipe tapped into the suction, and carried to the top of the separation-box. A plug-valve is attached to the end; the agitator draws air through this pipe, and is controlled by setting the valve. In order to make this adjustment easy, the plug in this valve is not tapered and the hole consists of a slot $\frac{1}{16}$ in. wide and $\frac{1}{2}$ in. long.

The agitators of this section consist of ordinary centrifugal pumps, the runners having three arms set at 60° and revolving at 960 revolutions per minute.

The separation-boxes are similar to those of the lead section, and the valves for controlling the flow are the same. There are six of these boxes. The agitators are driven in pairs by means of a belt off the main shaft; this shaft is driven by a 100-hp. motor.

The zinc floats rapidly. The head in the separation-boxes ranges from 36 in. deep in the first four to 18 in. in the fifth, and the sixth is kept overflowing slightly. This overflow is sent to the zinc-middling Dorr thickeners for re-treatment.

The acidity of the pulp as it discharges from No. 6 pan is kept at about 0.08%, as the tailing is cleaner with this acidity than with a lower one. The discharge from No. 6 pan is through a 5-in. cast-iron pipe to two 25-ft. Dorr thickeners 10 ft. deep; the arms on these make one revolution in two minutes. The overflow from these thickeners passes in a launder to the zinc-section solution-tanks, where it is kept up to temperature by having steam blown into it. The tailing-discharge, from the bottom, delivers to an elevator that raises it to a small box to which two lines of 4-in. piping are fixed. These pipes carry the pulp to the tailing-dams. Only one is used at a time, the other

being kept ready in case of a choke. High-pressure water is connected to these pipes so that in case of their becoming blocked they can be readily cleared again.

The zinc concentrate overflowing from these separation-boxes passes to a common launder delivering to a small elevator. This raises it to a height sufficient for it to flow down a launder to the zinc re-treatment plant, where it is delivered into a small mixer at the head, similar to those previously described. Here it is diluted down to an 8% pulp and re-floated in three separation-boxes.

Everything in this plant is similar to that on the first zinc section, except that the agitators are direct-coupled to motors. The first two have a 30-hp. motor placed between them, and the third is coupled to a 15-hp. motor. Very little acid is required in this section, there being hardly any acid-consuming material present. The acidity of the pulp is kept at 0.1% approximately.

The discharge from the third box passes to a 25-ft. Dorr thickener 10 ft. deep; the arms on this make one revolution in two minutes. The overflow from this passes to a storage-tank from which it is pumped to the small mixer at the head of the separation-boxes. Steam is blown into the solution-tank in quantity sufficient to keep the temperature at 125° F. The discharge from the bottom of the thickener passes to the elevator taking the drainage from the first zinc-float section, and this delivers it to the zinc-middling thickeners for re-treatment.

The final zinc concentrate from the three re-treatment boxes flows in a launder to a vat on the ground-level. This vat, 20 ft. diam. and 5 ft. deep, is fitted with arms revolving at 14 r.p.m. to keep the solids in suspension. When this vat becomes full it is pumped out to the zinc-storage dams.

The floor under each section of the plant is concreted and faced with cement, and is in the form of a large spoon-drain. That under the lead section falls to an elevator, which takes any leakage with any material discharged from the bottom plugs of the separation-boxes, and returns them to the first mixer, from which it passes with fresh dump-slime through the tube-mill to the feed-storage vat.

The floors under the first zinc-float section and the re-treatment section both fall to a common elevator. Any leakage or discharge from the bottom plugs of these boxes passes to this elevator, together with the discharge from the re-treatment Dorr thickener, and are returned to the two 30-ft. diam. zinc-middling Dorr thickeners. By this means any slime accumulating on the floor can be readily cleaned up by washing with a jet of water.

The sulphur-burners are of simple construction. They consist of two cast-iron pipes, 20 in. diam. and 10 ft. long, laid on the ground. The two ends are closed by means of pieces of boiler-plate secured by bolts. Through one end of each a hole 1¼ in. diam. is bored, slightly above the centre of the pipe; this hole is to admit air. The other end of each burner is coupled to a 3-in. cast-iron pipe into which the burner-gas delivers. This connection is made as near the top of the end plate as possible.

A 4-in. cast-iron pipe is coupled on to the top of each burner near the end that the air enters. This pipe supplies the means of charging the sulphur, and is kept closed by means of a piece of plate and insertion-joint held in place by two bolts. The 3-in. pipe passes to a receiver made of cast-iron. This is 3 ft. diam. and 8 ft. high; it condenses most of the sulphur that may be volatilized accidentally.

From the top of this receiver a 3-in. wrought-iron pipe is carried up to the top of the plant, and then along the entire length of the lead-section. Into this pipe the 1-in. pipe leading to each agitator is connected. The smaller pipes, one inch and one-half inch, are fitted together with unions so that they can be readily taken apart and cleaned in case they become blocked. The sulphur burnt amounts to 1 to 1.3 lb. per ton of slime treated.

The supply of acid for the plant is run from the acid plant to the main tank through a 1-in. lead pipe; this tank is placed at the highest point of the plant, and the acid can be drawn from it to the three smaller tanks placed close alongside the small mixers at the head of each section. All these tanks are fitted

with overflows leading to a large tank on the ground-level. By opening a valve in the bottom of any of the elevated tanks the acid can be run to this tank; the arrangement is convenient, and repairs can be readily effected at any time.

The principal points that require careful watching are as follows:

(1) That the temperature of the pulp at the head of the lead section does not rise above 90° F. If it does, the zinc has a tendency to float and seems to crowd out the lead.

(2) That the pulp on the lead section does not rise above 27% solid by weight. Higher pulps result in low-grade lead concentrate and incomplete recovery; this, of course, means low-grade zinc.

(3) That too much hyposulphite is not used. If more than 3 lb. per ton is added, it causes the zinc to be slow in floating in the zinc section and makes a high tailing.

(4) That the acidity of the pulp on the lead section does not rise much above 0.03%, as this has the same effect as too high a temperature. If the solution becomes neutral, the lead concentrate falls in grade owing to gangue passing over with it. In practice no trouble is experienced in maintaining any of these conditions.

(5) That the SO_2 pipes do not become choked. The SO_2 keeps the lead clean, and a choked pipe generally shows itself in the color of the lead flowing from the separation-box. Choked pipes also increase the power required to drive the agitators. The chief cause of this trouble is volatilized sulphur, due to excessive heat in the burners. This can be checked by having a few holes in the 3-in. SO_2 main, which, if the temperature of the burner starts to rise unduly, can be opened; air will then be drawn in through these and less through the burner, thereby checking the combustion.

The assay of the material being treated is as follows:

Zinc	16.5%
Lead	12.8%
Silver	15.5 oz.
Oxidized lead	4.7%

Sizing-tests on the feed give:

Plus 150	8.0%
Plus 200	5.5%
Minus 200	86.5%

The lead concentrate contains:

Zinc	8.0%
Lead	63.0%
Silver	84.0 oz.

The zinc concentrate contains:

Zinc	50.0%
Lead	4.0%
Silver	13.0 oz.

The tailing contains:

Zinc	2.0%
Lead (total)	8.0%
Silver	4.2 oz.
Oxidized lead	7.0%

The agitators in this plant run for five weeks, when they require new lining-plates and new runners. Between 14,000 and 15,000 tons of slime passes through the agitators in this time. From three to four agitators are changed weekly. The elevators have to be overhauled every week, and the slide-valves over the discharge-pipes of the separation-pans have to be seen to weekly. The slides are made so that they can be turned upside-down, and when one end is worn it is turned top-to-bottom and then runs for another period. These constitute the main repairs.

Small-scale tests indicate that the oxidized lead now passing out with the tailing can be readily re-sulphidized and recovered together with the silver, reducing the assay of the residue to about 1% lead and 1 oz. silver per ton. A plant is now being designed to do this.

THE FLOTATION OF GALENA AT THE CENTRAL MINE, BROKEN HILL [1]

By R. J. Harvey

Introduction.[2]—The ore is a complex silver-lead-zinc sulphide associated in the main with quartz, rhodonite, rhodochrosite, and some garnet-sandstone. The assay-value is now approximately 11 oz. silver, 14% lead, and 15% zinc. The silver accompanies the galena. The lead is present as a good-grade galena and the zinc as a somewhat low-grade blende not assaying much better than 50% zinc. Crushing to 40-mesh has been found necessary to obtain complete freeing of the mineral particles from the matrix and from each other.

In brief, the milling operations prior to the introduction of selective flotation were:

Crushing to $\frac{1}{8}$ inch and jigging.

Re-grinding the jig-tailing to 40-mesh.

Concentration on Card and Wilfley tables, and Weir-Meredith vanners, the former for the grainy material and the latter for the slime.

Flotation for a leady-zinc concentrate that was re-tabled on Wilfley tables and Weir-Meredith vanners produced an improved grade of zinc concentrate and gave a little more lead concentrate. See Fig. 1.

In 1902 or 1903 it was a matter of common observation that, wherever there was a splash of pulp with the consequent aeration, bubbles of air were formed carrying galena, and at one period boys were employed to skim off this froth, which was added to the concentrate before shipment.

[1] From the *Mining and Scientific Press* of February 1, 1919.

[2] A paper read before the Institution of Mining and Metallurgy, London, on November 21, 1918.

The milling results of the above operations were:

	Proportion, %	Silver, oz.	Lead, %	Zinc, %	Recovery		
					Silver, %	Lead, %	Zinc, %
Crude ore	100.0	11.6	14.5	16.4	....	....	....
Lead-mill lead concentrate	15.5	32.9	67.6	6.2	43.9	72.1	5.8
De-leading lead concentrate	1.3	46.3	60.6	13.8	5.3	5.5	1.1
					49.2	77.6	....
Zinc concentrate	30.8	16.1	8.3	45.8	42.6	17.7	85.8
Residue	....	2.3	1.8	2.9	....	....	....

Effective lead recovery 77.6%
" zinc recovery 85.8%
" silver recovery 49.2%
Tonnage treated: 4000 long tons per week.

The introduction of flotation as a commercial process for the recovery of blende caused the matter, however, to be dropped for the time and no more was done in the direction of galena flotation until the middle of 1913, when the first serious attempt to do so was made. This comprised the erection of a plant on the systems devised by F. J. Lyster and T. M. Owen, and involved aeration aided by the use of an essential oil, namely eucalyptus. This operated on slimes and demonstrated the possibilities of the selective flotation of galena.

About the same time the then mill-superintendent, A. W. Wincey, designed a crowding-hood on a distributing-box that received the discharge of an elevator carrying pulp, and by this means was able to obtain without cost about 15 tons weekly of a float-lead concentrate rich in silver. This further confirmed the feasibility of selective flotation.

Experimental Work.—The use of selective flotation and its evident great bearing on the possible profits from the company's operations determined the management to erect an experimental laboratory where flotation methods suitable to the ore could be evolved. I was appointed experimentalist in this laboratory.

The first important investigation carried out was to determine the possibility of recovering the valuable metals from a large dump of slime, all of which was ten years old. This dump represented the slime accumulated during several years before the flotation process was in use on the mine.

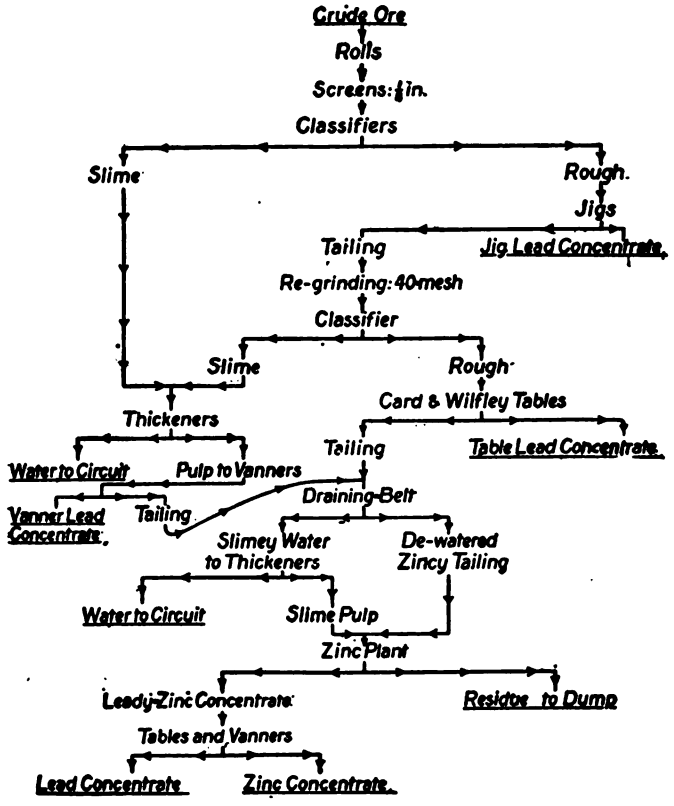


FIG. 1.

After some experiments, I found it possible to obtain a fair recovery of fine argentiferous galena by flotation, using only sulphuric acid as a medium, the results, however, being improved by performing the operation in a flotation circuit (water already used for flotation purposes). This, with the apparatus, was patented in the names of James Hebbard (the manager of the mine)

and myself, and assigned to Minerals Separation, Ltd. Following these results an already existing plant was altered to suit the new conditions and commenced operations early in 1914. A description of this plant, the flotation machine of which was the outcome of experiments conjointly carried out by the Broken Hill South Silver Mining Co., Amalgamated Zinc (De Bavay's), Ltd., and the Sulphide Corporation, follows later.

While this dump-slime investigation was proceeding, tests were made upon current slime production in the same apparatus, using eucalyptus in place of acid, and indications were obtained of the possibility of future success.

Dump-Slime Plant.—It has already been stated that this plant started operations after re-modeling early in 1914. Previously it had been used quite successfully to treat the dump-slime making a leady-zinc concentrate, which, however, was not readily marketed, and in consequence in 1909 the plant was stopped and has not since been in operation. The plant lay some distance from the slime-dump, and this involved haulage by rail. Hopper-wagons with bottom-discharge were used. The material was shoveled, after discharge from the wagons, onto a belt-conveyor and fed to a pair of grinding-pans adapted as Chilean mills. After thorough pulping, it was elevated to a set of six mixer-boxes. These boxes, of cast-iron, 3 ft. 6 in. square and 5 ft. deep, were of the under-driven sub-aeration type. The stirrer, which was 18 in. diam. and 3½ in. deep, acted both as agitator and air-pump and ran at a peripheral speed of 2300 ft. per minute.

Immediately before the pulp reached the first box, sulphuric acid was added. Lead concentrate was removed from the first four boxes, the float from the last two being returned to the feed. Flotation for the remaining valuable metals followed, using acid, eucalyptus, and steam sufficient to raise the pulp to 130° F. The leady-zinc concentrate obtained by this second flotation operation was passed over Krupp tables and Weir-Meredith vanners to induce a further separation of the galena from the blende. It was not expected that the selective flotation would

recover all the galena, but that it would catch the finest of the lead unobtainable by ordinary gravity concentration.

It must be remembered that the slime being treated was accumulated in days when classification apparatus was not so effective as it is today, and, consequently, quite coarse galena existed in the dump. The pulp would practically all pass 200-mesh, but galena of this size is obtained associated with larger sizes both on a jig and on a table.

This plant (Fig. 2) was in operation with improving results until war broke out in August, 1914, when it was once more stopped and has since remained so. The following table shows the work being done immediately prior to closing-down:

	Proportion, %	Silver, oz.	Lead, %	Zinc, %	Recovery		
					Silver, %	Lead, %	Zinc, %
Feed	100.0	15.6	17.0	19.1	....	....	....
Lead concentrate by flotation	10.3	53.8	49.9	21.4	35.5	30.1	11.6
Lead concentrate on tables	4.2	35.2	60.4	14.5	9.6	15.0	3.2
Zinc concentrate	30.2	17.5	15.2	41.7	33.9	26.9	65.9
Residue	....	5.9	8.6	6.7	....	....	....

Lead-Mill.—It has already been remarked that experiments demonstrated the possibility of recovering galena from the slime produced in the lead-concentrating mill. Early in 1915 it was decided to apply sub-aeration methods to this slime in preference to the Lyster system. For a start, an 8-box machine was erected. This was similar in design to that used at the dump-slime plant, but smaller. Wooden boxes 24 by 24 in. by 36 in. high were supplied with 10-in. stirrers driven from below at a speed of 1000 r.p.m. The air was drawn by the stirrers through ½-in. pipes supplied with regulating valves. Two horse-power was required per stirrer. To control the rate of feed to the boxes a feed-tank was installed. As this 8-box unit gave satisfactory

results, two more similar units were erected, and the 24 boxes were then capable of handling the full output of slime, some 800 tons weekly. This plant used the ordinary mill-circuit, a mixture of mine-water and excess water from the existing zinc-flotation plant, with addition of Broken Hill Water Supply Co.'s water when required.

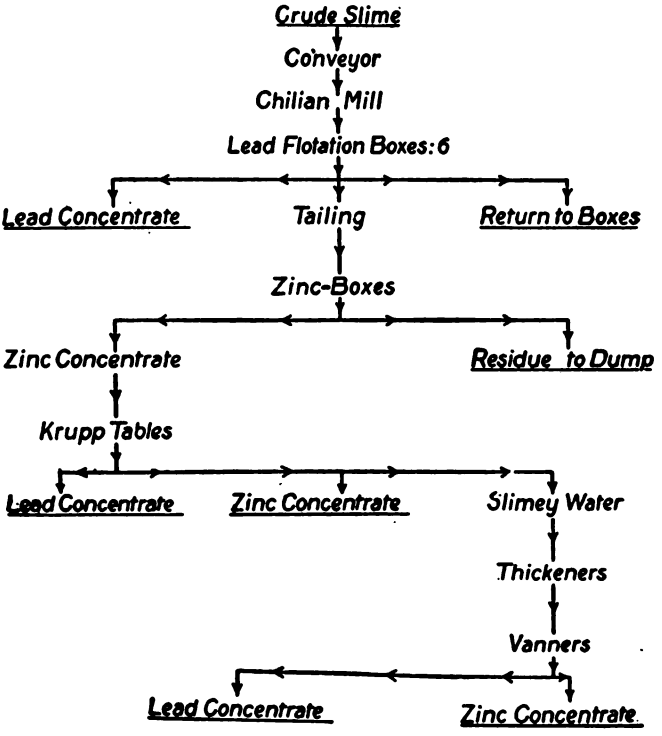


FIG. 2.

As flotation media, eucalyptus oil, wood-tar oil, and pine-oil were used, being added to the feed-tank elevator. No definite mixture of these was supplied, the quantity of each being regulated by requirements for the time being. The amount used per ton of slime averaged 0.25 lb., and wood-tar oil predominated.

The following table gives the results obtained by this plant:

	Proportion, %	Lead, %	Recovery of Lead, %
Slime feed	100.0	13.3	....
Lead concentrate	13.3	67.1	67.1
Tailing	86.7	5.0	....

So much less fine galena was now going to the zinc-flotation plant and thence to the zinc-concentrate de-leading section that it was possible to put the Weir-Meredith vanners in the latter section out of commission, still, however, retaining the Wilfley tables.

For some time prior to 1915 it was evident that a saving in cost and an enhanced recovery could be obtained by the erection of a new zinc-flotation plant. Work in the experimental plant had demonstrated that sub-aeration methods would be satisfactory, and a plant for this purpose was designed, erected, and in October, 1915, was put into operation. While experimenting, it was found that fine galena could be recovered by flotation from the by-products of the lead-mill. Here it should be mentioned that the flow-sheet then in use did not provide for quite all the slime to go to the selective plant (24 by 24-in. boxes). The Card and vanner tailings were de-watered by means of a draining-belt, the de-watered material containing some settled fine going to the zinc-plant, and the slimy water to thickeners. The settled slime from the latter provided the feed for the selective plant, the tailing from which went to the zinc-plant, which in one section handled the whole of the zincy tailings (coarse and slimes) of the lead-mill, which handled 4000 tons per week of 136 hours. The flow-sheet (Fig. 3) will help to make matters clear. In view of the presence of this recoverable galena in the feed to the zinc-plant it was decided to make the new plant a combined lead and zinc-flotation plant, that is, capable of first floating off the galena and subsequently the blende. This dual machine was of the same design as that at the dump-slime plant with boxes 42 by 42 by 60 in. high. Five boxes were set apart for galena flotation and nine for zinc—14 boxes in all.

SIZING ANALYSIS, ZINC CONCENTRATE AFTER THE INSTALLATION OF GALENA FLOTATION

I. M. M. Screens.	Proportion, %	Silver, oz.	Lead, %	Zinc, %
Bulk.....	....	12.2	4.6	47.3
+ 40.....	6.7	8.8	3.0	50.2
− 40+ 60.....	22.0	11.4	4.2	48.4
− 60+ 80.....	20.0	11.4	4.5	47.6
− 80+100.....	11.6	12.0	5.0	46.6
−100+120.....	4.2	11.2	3.8	47.0
−120+150.....	6.2	11.2	3.5	47.2
−150+200.....	5.0	11.8	4.7	47.4
−200	24.2	14.2	6.0	45.4

The marked success of the above changes in the milling operations and the evident possibility of floating the slimed galena naturally led to seeking means of concentration of coarser particles of galena by flotation. Two metallurgists on an adjacent mine, H. V. Seale and W. Shellshear, had utilized the principle of the nozzle for aeration of a flotation pulp, and had designed an apparatus that was capable of floating coarse galena. Their idea was modified by others on the staff of the Zinc Corporation and was then tried by the management of the Central mine. A plant to treat 2000 tons per week was erected and after experiments a successful design was evolved by the metallurgical staff of the Central mine. So satisfactory was the design and so encouraging were the results obtained that it was decided to erect a plant large enough to handle the whole output of re-ground jig-tailing previously treated on Card tables. This new plant has recently been completed and is now in operation with good results; in fact, it is hoped that in the end it will be possible to discard the five boxes in the zinc-plant that are now used for floating galena. A small quantity, about 2 oz. per ton, of a mixture of coal-tar and eucalyptus is added to the pulp as flotation media.

The following comparative tables show the recovery made by the Card tables and that obtained with the Cascade machines:

	Proportion %	Silver, oz.	Lead, %	Zinc, %	Recovery		
					Silver, %	Lead, %	Zinc, %
By-products from jigs.....	...	10.6	10.0	16.1	....	....	....
Table concentrate.....	5.4	38.6	63.5	8.0	19.6	34.4	2.7
By-products from tables...	...	9.0	6.9	16.5	....	....	....
By-products from jigs.....	...	9.7	8.9	16.6	....	....	....
Cascade concentrate.....	6.6	46.2	63.9	11.6	31.4	47.3	4.5
By-products from Cascades	...	7.1	5.0	17.0	....	....	....

Lead-Cascades.—This is the name given to the latest galena-flotation plant of the Central mine, which has ousted the Card tables previously in use. The plant is simplicity itself (Figs. 4, 5, and 6). There are no moving parts, no use of compressed air. All that is required is the necessary elevating of prepared pulp. On a suitable site this elevating would not be required. The plant consists of a series of boxes set one above the other, the pulp in descending from box to box passing through nozzles, thereby drawing into itself the air necessary for flotation. The concentrate flows over the lip of each box and the tailing passes to the next in series. The boxes are 36 in. long, 18 in. wide, and 28 in. high. Three nozzles are supplied to each box. The distance between the bottoms of any two boxes is 4 ft. 9 in., and nine boxes of the above size in series form one unit. In order to reduce the height of the plant and bring it on to as few floors as possible, there is an elevator between No. 4 and 5. Two units are in use, the intermediate elevator being common to both. By means of a system of overflows, irregularities in the volume of pulp are checked. This plant has been a complete success, the recovery of the lead and silver being greater than with Card tables, and no Card tables are now in use for concentrating crushed ore. The galena that escapes the Cascades is, if fine, caught by the galena-flotation boxes in the zinc-plant and, if coarse, is removed from the zinc concentrate by the Wilfley tables in the de-leading plant.

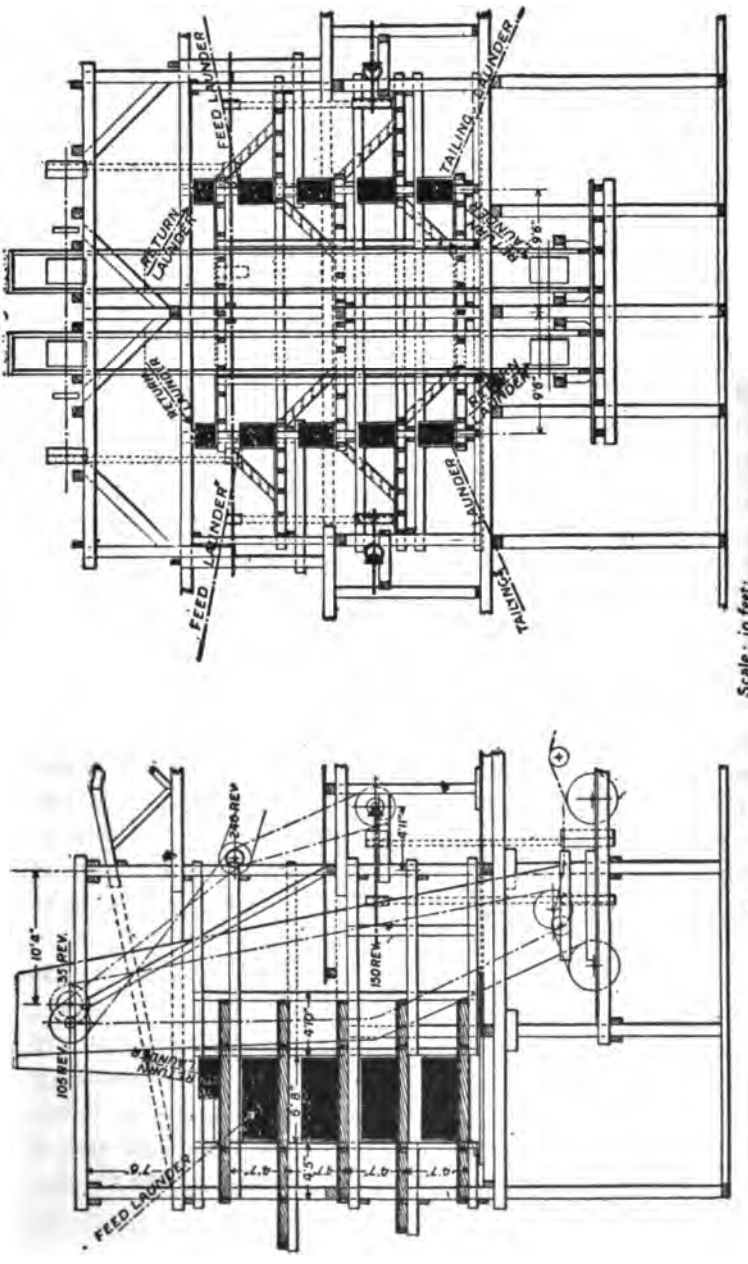

FEED LAUNDER
RETURN LAUNDER
TAILING LAUNDER
SIDE ELEVATION
END ELEVATION
Scale: in feet:
0
5
10
20
30
40

FIG. 4.

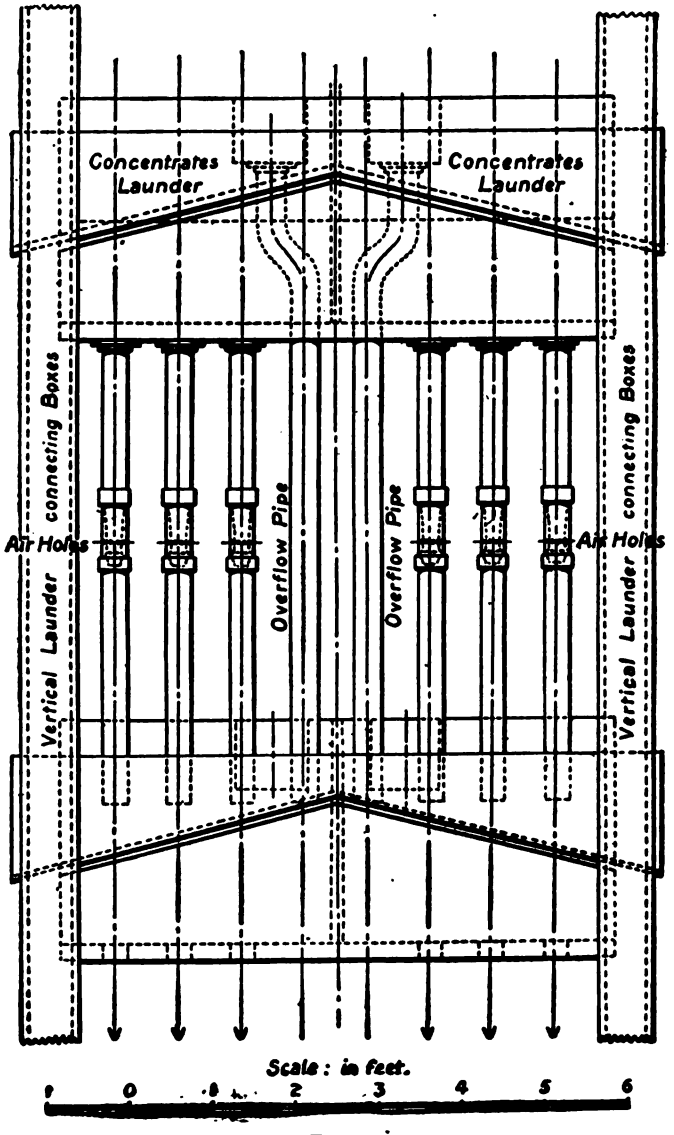

Concentrates Launder
Concentrates Launder
Vertical Launder connecting Boxes
Air Holes
Overflow Pipe
Overflow Pipe
Air Holes
Vertical Launder connecting Boxes
Scale : in feet.
1 0 1 2 3 4 5 6

FIG. 5.

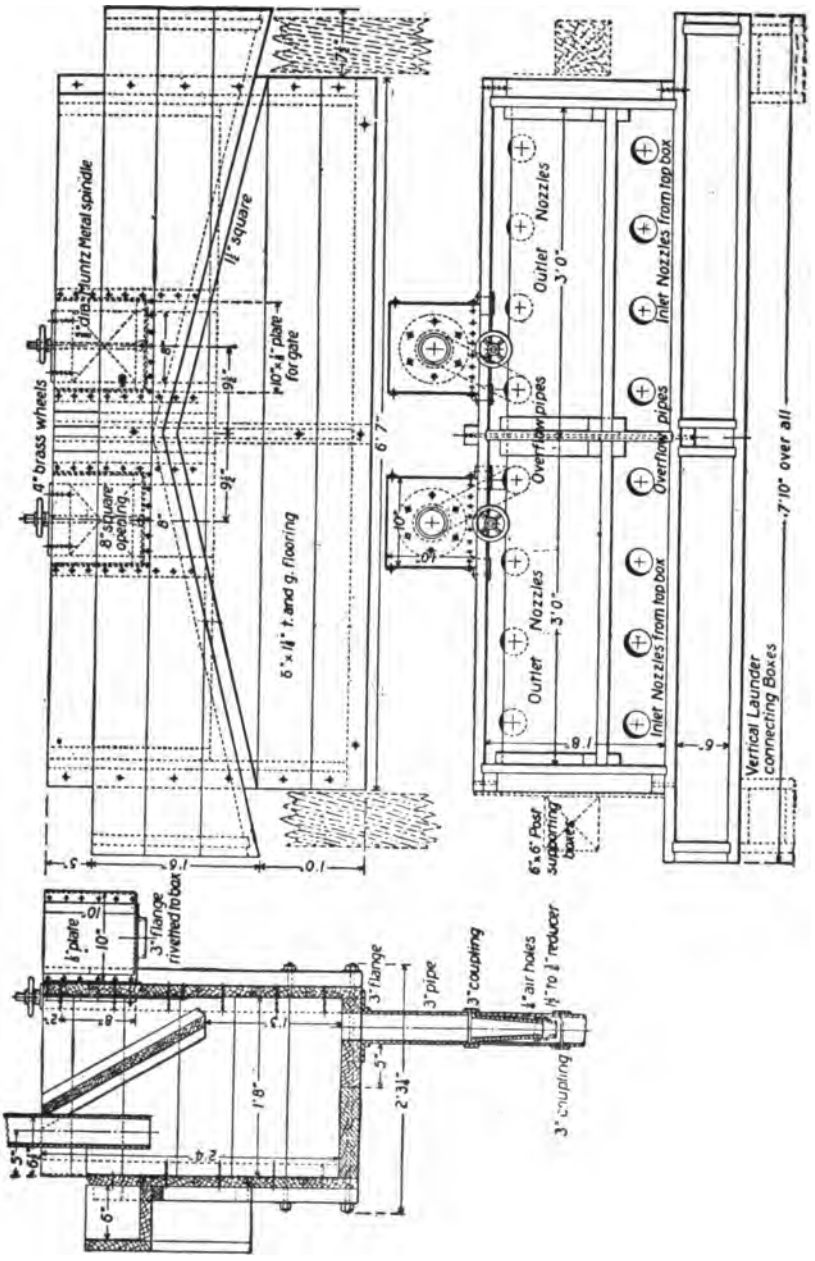

Outlet Nozzles
Inlet Nozzles from top box
Overflow pipes
Vertical Launder connecting Boxes
7'10" over all
6"x6" Post supporting boxes
11" square
6"x 1/4" t. and g. flooring
4" brass wheels
8" square opening
10"x 1" plate for gate
1" plate
3" flange riveted to box
3" flange
3" pipe
3" coupling
1" air holes
1" to 1" reducer
3" coupling
1'8"
2'3"

FIG. 6.

The following shows the milling results for a recent period:

	Proportion, %	Silver, oz.	Lead, %	Zinc, %	Recovery		
					Silver, %	Lead, %	Zinc, %
Crude ore	100.0	11.8	14.0	15.6	....	....	....
Lead-mill lead	17.4	40.8	64.6	9.0	60.1	80.2	10.0
De-leading lead	1.3	39.3	58.1	13.8	4.3	5.4	1.1
					64.4	85.6	
Zinc concentrate	27.2	12.8	5.1	47.9	29.4	9.9	83.3.
Residue	....	1.3	1.1	1.5	....	....	....

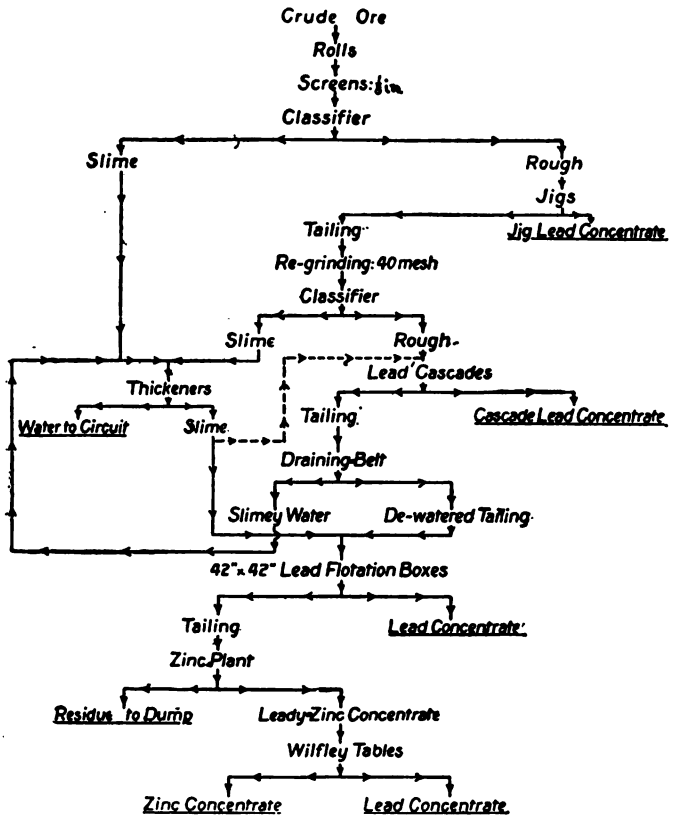


FIG. 7.

Effective recovery, lead 85.6%, silver 64.4%, and zinc 83.3%.

In conclusion, I may say that the problem is not completely solved, perhaps it never will be, but scientific investigation is proceeding all the time. The substitution of flotation for gravity concentration has meant the discarding of 20 Card tables, 4 Wilfley tables, and 16 Weir-Meredith vanners in the lead-mill, and of 14 Weir-Meredith vanners in the de-leading plant, with the necessary attendants and maintenance, and it has simplified the flow-sheet of the Central mill. (Fig. 7.)

Screen-analysis of jig-lead concentrate, Card-table lead concentrate, and Cascade lead concentrate are appended, as they are instructive and of some interest in conjunction with the foregoing history.

The object of this paper being almost entirely to trace the steps by which flotation has superseded gravity concentration at the Central mine, the various mechanical contrivances tried or adopted have not been elaborated, hence no machine-drawings are appended.

The Sulphide Corporation, owning the Central mine mentioned above, has paid large dividends since 1898, 25% in 1917. The output last year was 41,426 tons of concentrate assaying 40.9 oz. silver, 63.1% lead, and 8.9% zinc, and 55,990 tons containing 12.6 oz., 5.7%, and 47.3%, respectively.

SIZING-ANALYSIS, JIG-LEAD CONCENTRATE

I. M. M. Screens.	Proportion, %	Silver, oz.	Lead, %	Zinc, %
Bulk.....	....	33.8	64.2	6.5
+ 40.....	43.8	37.6	68.4	7.3
− 40+ 60.....	13.4	35.2	70.0	4.0
− 60+ 80.....	15.0	32.4	66.8	4.3
− 80+100.....	7.5	26.6	60.8	6.0
−100+120.....	3.4	27.2	58.2	5.8
−120+150.....	5.9	24.8	51.4	7.4
−150+200.....	3.1	27.2	55.0	7.9
−200	7.8	30.2	54.8	9.3

SIZING-ANALYSIS, CARD-TABLE LEAD CONCENTRATE

I. M. M. Screens.	Proportion, %	Silver, oz.	Lead, %	Zinc, %
Bulk	....	33.4	63.8	4.6
+ 40	0.5	....	30.6	14.0
− 40+ 60	3.2	56.2	48.6	8.3
− 60+ 80	6.4	39.6	56.6	5.5
− 80+100	10.3	35.0	59.2	4.7
−100+120	7.6	32.0	59.4	4.4
−120+150	9.2	30.8	59.4	4.6
−150+200	17.9	30.6	61.2	4.8
−200	44.9	32.4	69.6	4.0

SIZING-ANALYSIS, CASCADE LEAD CONCENTRATE

I. M. M. Screens.	Proportion, %	Silver, oz.	Lead, %	Zinc, %
Bulk	....	46.9	61.0	13.3
+ 80	4.2	65.6	39.4	24.3
− 80+100	7.1	51.4	50.0	19.1
−100+120	5.0	47.4	52.0	18.1
−120+150	11.6	44.8	55.8	16.3
−150+200	9.6	43.2	60.4	15.1
−200	62.5	45.8	65.8	11.2

RECOVERY OF COPPER FROM FLOTATION BY LEACHING [1]

By Percy R. Middleton

The use of the flotation process for the treatment of low-grade copper ores has introduced an additional problem in the form of smelting the finely divided concentrate resulting from the operation. The majority of Australian mining companies that adopted the flotation process were equipped with blast-furnaces and consequently some method of sintering had to be adopted before the concentrate could be successfully smelted. Under Australian conditions the cost of sintering is high, and considerable trouble has been experienced in obtaining a satisfactory product. The smelting and railroad facilities of the United States seem to have caused the American mining companies to overlook the fact that an increased profit could be made by treating the concentrate on the ground in preference to shipping it to the smelter.

It is well known that the sulphides of copper can be converted into the sulphate by roasting, and if the right conditions are maintained, from 85 to 90% of the copper may be turned into a water-soluble salt. Utley Wedge gives particulars of experiments on the sulphatizing roasting of copper ores and concentrates, in the Transactions of the A. I. M. E., Vol. XLIV (1912), and in view of his results it is hard to understand why more attention has not been given to this subject. Mr. Wedge conducted his experiments in a muffle-furnace, but I have found no difficulty in obtaining satisfactory results in the ordinary type of roasting-furnace. To obtain a satisfactory sulphatizing roast,

[1] From the *Mining and Scientific Press* of June 7, 1919.

skill and a thorough knowledge of furnace conditions are required; the cause of failure hitherto has been lack of the essential skill and knowledge of how the roast should be conducted. As in the majority of metallurgical operations, no fixed method can be applied to all ores. A wide variation in range of temperature will be found necessary to obtain the best results. I have made a special study of this subject and have roasted over one thousand tons of various ores and concentrates.

The recovery of the precious metals from the leached residues may appear at first to present insurmountable difficulties, but on investigation these disappear. Things that were impossible ten years ago, owing to the lack of apparatus, are now practicable. The improvement in mechanical appliances, for example the vacuum-filter and the Dorr decantation system, has made commercially possible many processes that were formerly regarded as metallurgical curiosities. The extraction of copper after roasting and leaching is usually so complete that the cyanide process may be applied for the recovery of the gold and silver without excessive consumption of cyanide, or the gold may be recovered by chlorination and the silver by either sodium hyposulphite or brine. Laboratory experiments have shown satisfactory results with cyanide; however, it is an open question whether the advantage of using one solution for the recovery of both gold and silver would offset the danger of incomplete washing in a large plant. A good extraction of gold has been effected with chlorination in large-scale tests, but the ore on which the experiments were conducted carried practically no silver; on the other hand, laboratory experiments show that after chlorination the silver is in a condition suitable for extraction by either sodium hyposulphite or brine.

At the conclusion of some experimental work on the leaching of low-grade sulphide ores for the Mt. Lyell M. & R. Company, in Tasmania, I suggested the roasting and leaching of the flotation concentrate and was instructed by this company to carry out a complete investigation. Similar work was conducted for other Australian mining companies and in each case satisfactory results were obtained.

The following is a summary of some of the results of the above investigations:

Concentrate No. 1.—Assay: Cu 9.11%, Fe 26.7%, S 29%.

This sample was roasted at a temperature not exceeding 600° C., the product being leached with 5% sulphuric-acid solution, with the following results:

Weight of sample before roasting, 1000 gm.; copper, 9.11%. Roasted product leached with two litres of 5% sulphuric-acid solution. Resulting solution contained 45 gm. copper per litre.

Copper extracted, 90 gm., or 98.7%.

Concentrate No. 2.—Assay: Cu 20.52%, Fe 28.2%, Au 1.81 oz.

Roasted at a temperature not exceeding 650° C.

Weight of sample before roasting, 1000 gm.; copper, 20.5%. Roasted product leached with two litres of 5% sulphuric-acid solution. Resulting solution contained 100.44 gm. copper per litre.

Copper extracted, 200.88 gm., or 97.9%.

Concentrate No. 3.—Assay: Cu 5.8%, Fe 35.0%, and Au 0.587 oz.

Roasted at a temperature not exceeding 650° C.

Weight of sample before roasting, 1000 gm.; copper, 5.8%. Roasted product leached with two litres of 5% sulphuric-acid solution. Resulting solution contained 28.0 gm. copper per litre.

Copper extracted, 56 gm., or 96.5%.

Cyanide tests for the recovery of gold were conducted on the residue from the No. 2 and 3 leaching experiments. The residues were given a lime wash and then treated with cyanide solution. The copper present did not interfere with the gold extraction, no trace of troublesome cyanicides being detected. The average gold extraction over a number of tests was 90% and the consumption of cyanide about 1.5 lb. per ton of residue treated. Chlorination also gave satisfactory results when the acid-soluble iron in the roasted product was below 1%. In order to confirm the copper extraction obtained in these laboratory experiments, a bulk-test was conducted under actual working conditions in the Edwards metallurgical works, at Ballarat, Victoria. The roasting was performed in a 7-panel duplex Edwards furnace

and the product was leached by percolation in vats fitted with filter-bottoms. Scrap-iron was used to precipitate the copper. The furnace was operated continuously at a temperature of about 650° C. The roasted material was dampened with water before being charged by hand into the leaching-vats, about 20 tons forming the charge, which was covered with a 5% solution of sulphuric acid; after 24 hours contact, this solution was drawn from the bottom of the vat into a launder connecting with the precipitation vats. The charge was then washed free from copper with water, which also went to the precipitation vats. In the above manner 110 tons of concentrate was roasted and leached with the following results: the tonnage treated was 110 tons of concentrate containing 7.6% copper, and the copper produced amounted to 19,856 lb. cement copper assaying 80% Cu, showing an extraction of 95%.

This bulk-test was conducted with the object of determining whether the concentrate could be roasted with satisfactory results on a working scale and did not include any experimental work on precipitation. The fact that copper can be commercially recovered from sulphate solutions by electrolysis has been established beyond dispute at Chuquicamata, in Chile, and at Ajo, in Arizona. The electrolytic deposition of copper from solutions resulting from the leaching of roasted ore is the ideal method of precipitation, as sufficient acid can be regenerated to carry on the process, thus obviating the need for an expensive acid plant, and the amount of acid-soluble iron in the roasted product is under control, being regulated by the furnace conditions; therefore the amount of " bleeding " would not be as great as in the case of electrolyzing solutions resulting from the leaching of oxidized ores where there is no control over the amount of iron entering the electrolyte at each cycle.

In order to illustrate the possibilities of this process the following working-costs were compiled from figures obtained in working-scale tests: Assuming the concentrate to contain 12% copper, 9 oz. silver, and 0.25 oz. gold, and treating 100 tons per day the items of cost would be:

Roasting	$0.30	
Leaching	0.15	
Gold and silver leach	0.75	
Handling residues	0.10	
		$1.30
Electrolytic deposition:		
Power, 240 kw-hr. @ 1c	$2.40	
Labor, etc	0.70	
		3.10
Losses:		
5% of copper, 12 lb. @ 15c	$1.80	
Silver, 1 oz. @ $1.01	1.01	
Gold	0.50	
		3.31
Capital account (retirement of $300,000 in five years):		
$100 \text{ tons} \times 360 \times 5 = 180{,}000 \text{ tons} = \frac{300}{180}$		1.66
Net cost		$9.37

The smelter returns from such a concentrate would be approximately as follows:

12% copper = 240 lb. less 15 lb. = 225 lb. @ 15c. less 3c	$27.00
9 oz. silver @ 95% of $1.01 = 96c. × 9c	8.64
0.25 oz. gold @ $19.	4.75
Value of metals less smelter deductions	$40.39
Freight and treatment	12.00
Net daily returns per ton of concentrate	$28.39

Ratio of concentration, say, 3 : 1.

$\frac{\$2839}{100 \times 3} = \$9.46$ net return per ton of crude ore.

SUMMARY OF COSTS OF BOTH PROCESSES

Smelting:		
100 tons @ 240 lb. copper per ton, 24,000 lb. at 15c		$3,600
100 tons @ 9 oz. silver per ton, 900 oz. silver @ $1.01		909
100 tons @ 0.25 oz. gold per ton, 25 oz. gold @ $19		475
Total value of all metals		$4,984
Returns from smelter = 100 × 28.39		2,839
Costs and losses by smelting		$2,145
Costs and losses per ton of concentrate	$21.45	
Costs and losses per ton of crude ore	7.15	
Net returns per ton of crude ore	9.46	

Roasting and leaching:		
Total value of metals as above		$4,984
Costs and losses, 100 tons @ $9.37		937
Net returns by leaching		$4,047
Costs and losses per ton of concentrate	$9.37	
Costs and losses per ton of crude ore	3.12	
Net returns per ton of crude ore	13.49	

Difference in favor of roasting and leaching, $4.03 per ton of crude ore.

If the working-costs and losses for roasting and leaching are raised to $12 per ton, instead of $9.37, the net return per ton of crude ore is changed to $12.61 per ton, the difference in favor of leaching being $3.25 per ton of crude ore.

A plant to treat 100 tons of concentrate per day would consist of two 13-panel duplex Edwards furnaces, five Dorr counter-current thickeners for copper leaching, four Dorr counter-current thickeners for gold extraction. If chlorination were employed a vacuum-filter and another series of Dorr thickeners would be required for silver extraction. In each case the thickeners would be 15 ft. diam. based on a settling-area of four square feet per ton of roasted product. In addition to the above plant, electrical equipment would be required for the precipitation of the copper.

zinc, is that sulphates of copper form during roasting and cause trouble in the handling of the pulp calcine. At the same time the presence of a certain amount of copper sulphate in the pulp is also advantageous, the reason for which will be explained later.

Another treatment applicable to this ore was the electrolytic process. The only reason why this process was not tried at this time was because it was a method still in the experimental stage, the development of which would have entailed an expense unwarranted by the known reserves of the mine. The operators had foresight enough to see the possibilities of the electrolytic process, so that all equipment and buildings furnished for the Horwood process could be used to advantage in the electrolytic process in case they should decide to adopt it at a later date.

Tests with the Horwood process were so promising that it was decided to build a 300-ton plant, the construction of which was started in April, 1917. Enough of the plant had been completed in September to test the practicability of the process. In December the plant was shut down to provide storage for the concentrate to improve the flotation machines, to finish the dryer, and to alter the roaster. Being pioneers in the process as applied to copper-zinc ores, the management could obtain no outside experienced help, so that numerous unforeseen problems had to be solved by trial. Owing to the increase in freight-rates and the necessity for some important changes in the flow-sheet, and the general operation of the plant, the mill was shut down in June, 1918. Work was immediately begun on the construction of an Edwards cooler for the roasted product, a reverberatory furnace for the copper concentrate, and, in order to simplify the flow-sheet, a new preferential flotation unit was built, and a different style of flotation machine introduced. It was not expected that better results would be obtained with this machine, but that the cost of operation would be much less than with the Janney machines.

A start was again made in December, 1918, and all improvements came up to expectations, with the exception of the new flotation unit, which fell down entirely. To switch back to the old method of flotation would have entailed considerable ex-

pense, since practically everything in connection with the old system had been dismantled. With the drop in the price of the base metals, and recent developments and improvements in the electrolytic process, it was decided to adopt this method. Before the last shut-down, results with the Horwood process were almost entirely dependent on the roast obtained, but during the interval improvements were made in roasting so that there was absolute control of conditions. A mistake, however, was made in the method of flotation, and by going back to the old conditions of flotation it is known exactly what results might be expected with the Horwood process, as applied to this or similar ores.

The Ore.—The ore of the Afterthought mine as delivered to the mill has the following composition:

Silver	5.50 oz.	Lead	0.80%
Gold	0.03	Sulphur	18.80
Copper	3.10%	CaO	8.70
Zinc	16.80	Al_2O_3	1.00
Iron	9.30	Insol. (barite and silica)	24.30

The following is the approximate mineralogical composition:

Chalcopyrite	10%	Sulphides	45%
Pyrite	9		
Blende	25		
Galena	1		
Calcite	15	Gangue	55%
Barite	12		
Quartz and slate	28		

The specific gravity of the ore is high, being about 3.5. The collective concentrate has a specific gravity of 3.93.

Method of Treatment.—The ore is crushed to 2-inch ring and ground to pass 48-mesh; it is then subjected to flotation, producing a collective concentrate and a final tailing. The collective concentrate is thickened, filtered, dried, and roasted lightly. After cooling it is subjected to flotation again, this time producing a froth called the zinc concentrate and a tailing called the copper-iron concentrate. These concentrates are then filtered and dried.

The milling equipment is as follows:

Coarse and fine ore-bins.
One 15 by 30-in. Blake crusher.
One 9 by 18-in. Blake crusher.
Elevator and two conveyors.
Oscillating feeders.
Two No. 64½ Marcy ball-mills.
Two Dorr duplex classifiers.
Two 3-in. Krogh sand-pumps.
Two 4-in. Krogh sand-pumps.
One 30-ft. Dorr thickener.
Two 21-ft. Dorr thickeners.
Two 16-ft. Dorr thickeners.
20 Janney sub-aerated flotation machines.
Two 8 by 8-ft. Oliver filters.
Three 30 by 5-ft. cylindrical dryers.
One 25-ft. 9-hearth Skinner roaster.
One 60-ft. Edwards cooler.
Four 4-ft. 6-disc American filters.

The tonnage treated is a minimum of 275 per day, with a maximum of 400 tons. This produces about 150 tons of collective concentrate or a ratio of concentration of about 2 : 1. This collective concentrate when treated preferentially gives 60 tons of copper concentrate to 90 tons of zinc concentrate.

The Crushing-Plant is at the bottom of the mill, to allow of sufficient grade for the railroad from the mine. The ore is dumped into a 500-ton bin, from which it is drawn through a heavy rack-and-pinion gate, with counterweights to permit ease of operation. A grizzley-feeder was originally installed but owing to insufficient space it was rejected. After passing over a stationary grizzley with 2-inch openings, the ore is crushed to 3 inches by a 15 by 30-in. Blake crusher. The discharge is conveyed by a shaking-conveyor to a 9 by 18-in. Blake crusher. This conveyor replaced a shaking-grizzley, which proved a failure on account of the tough character of the ore, which breaks into pointed and angular pieces, tending to clog the grizzley. The discharge of the 9 by 18-in. Blake joins the material from the 2-inch grizzley

and is elevated 50 ft. in a 16-in. bucket-elevator to a 20-inch conveyor 220 ft. long and running at 400 ft. per minute on an incline of 20°. This conveyor discharges onto a cross-conveyor, which in turn discharges through a tripper into a 1000-ton ore-bin at the top of the mill. A shuttle-conveyor, originally ordered to take the place of the cross-conveyor, was held up on account of war orders. A sampling-plant was provided in the crusher-building, but, owing to the inability to obtain the equipment at the time, it was thought advisable to do the sampling ahead of flotation.

Grinding.—From the bins the ore is drawn through two oscillating feeders and is fed by short conveyors to two No. 64½ Marcy ball-mills each running in closed circuit with a Dorr duplex classifier. The classification is good. Each mill handles about 160 tons per 24 hours. Owing to the high specific gravity of the ore, the classifier is run at a speed of 30 strokes per minute. About 800 tons of material per day is returned to the mill by the Dorr classifier, making a total of about 1000 tons of material passing through the ball-mill in 24 hours. To each mill approximately 11 gallons of water per minute is added, and the water added at the mill-discharge and classifier amounts to 37 gallons.

The following is a typical screen-analysis:

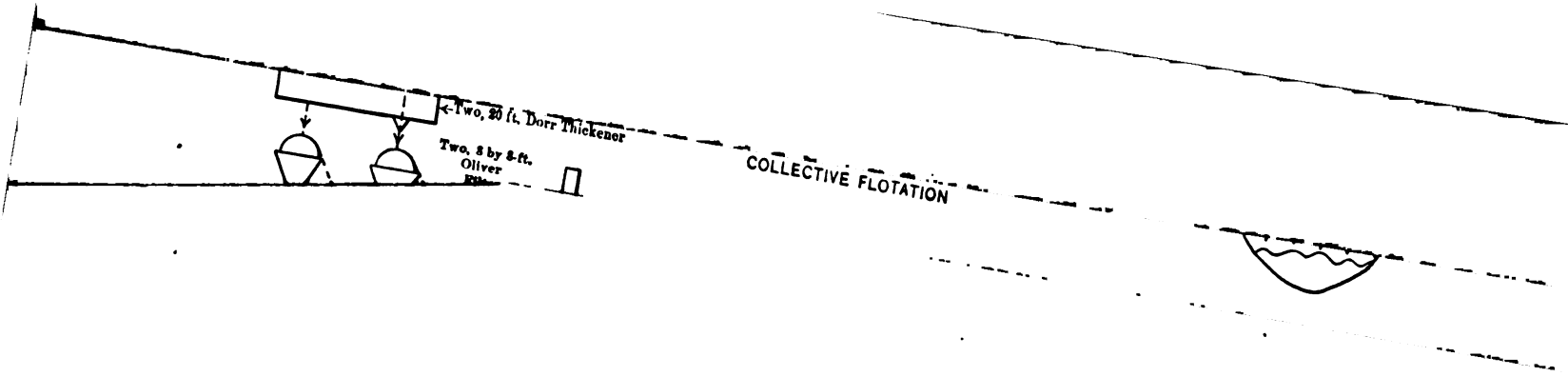
Mesh.	Ball-Mill Discharge 25.4% Water, 3.06% Cu, 17.8% Zn 953 Tons.		Classifier Overflow 65% Water, 2.86% Cu, 17.4% Zn 150 Tons.		Classifier Sand 15.6% Water 3.16% Cu, 20.4% Zn 803 Tons.	
	% Indiv.	% Accum.	% Indiv.	% Accum.	% Indiv.	% Accum.
Plus 10	6.14	6.14	.....	.....	7.58	7.58
10– 20	11.27	17.41	.....	.....	16.58	24.15
20– 30	12.30	29.71	.....	.....	11.18	35.34
30– 40	12.91	43.62	0.56	0.56	20.00	55.34
40– 60	15.30	58.92	4.43	4.99	15.16	70.50
60– 80	7.18	66.10	4.98	9.97	10.17	80.67
80–100	6.13	72.23	8.29	18.26	6.18	86.85
100–150	3.80	76.03	9.40	27.66	4.57	91.42
150–200	4.60	80.63	4.98	32.64	2.59	94.01
Minus 200	20.00	100.63	67.36	100.00	5.98	99.99

The reagents for collective flotation are added at the head of each ball-mill by means of disc-feeders. One Marcy mill is left-handed and the other right. Each is driven by a 125-hp. motor through a Lenox drive with endless leather belt. These drives give little or no trouble. Five-inch forged chrome-steel balls are used, and the mills operate at 28 r.p.m.

Collective Flotation.—After leaving the classifier the pulp is sampled automatically and then goes direct to 10 sub-aerated Janney machines, ten per unit. Each unit consists of seven roughers and three cleaners. There is ample room in the mill-building for another unit of flotation-cells. With the first equipment two Janney emulsifiers were used per unit; they were remodeled into cells similar to the standard Janney machine.

The flow is so arranged that concentrate may be taken direct from the first two Janneys and sent to the storage-tanks or it may go to the cleaners. The froth from the last two roughing-cells may go either to the cleaners or be returned to the head of the roughing-cells. The rough concentrate may be cleaned in three Janneys or cleaned in two and re-cleaned in a third. The tailing from the cleaners is returned to the head of the mill by means of three-inch sand-pumps arranged in duplicate. These pumps replaced an elevator, which gave considerable trouble on account of the accumulation of froth.

In all preliminary tests it was necessary to use acid, the consumption of which was prohibitive on account of the lime in the ore. Finally an oil (Barrett No. 609) was found that gave good results without acid; it had both collective and frothing qualities. This oil was the one most generally used during 1917 and the first part of 1918. It is undoubtedly a coal-tar creosote mixture containing some phenol, in cold weather throwing down a precipitate that is some naphthalene compound. Without this precipitate in solution the No. 609 oil gives poor results. Through small-scale experimentation with various oils it was found that a mixture of stove-oil with Pensacola No. 80 gave even better results, besides being a cheaper mixture. The oil is stored in a house above the mill and flows by gravity to the feeders at the ball-mills. Oils as well as other mill-supplies are


Two, 20 ft. Dorr Thickener
Two, 8 by 8-ft.
Oliver
COLLECTIVE FLOTATION

Drying and Roasting.—The filter-cake falls upon a belt-conveyor, which carries the concentrate to the drying-plant. The dryer is of the cylindrical type, 30 ft. long by 5 ft. in diameter. Oil is used for fuel. The attendance required is small, the filter operator having the dryer plant under his supervision. The dryer is efficient and the cost of drying is low. The average moisture in the dried product is 5%. Care must be exercised that it does not get below this, otherwise the discharge will be too hot, and not only cause trouble in feeding, but will tend to burn the belt-conveyor carrying the material to the roaster.

The dryer discharges into a 30-ton hopper. From this it is drawn by a plunger-feeder onto the roaster belt-conveyor. . The plunger-feeder replaced one of the disc type, as the hot concentrate tended to flow and give an unsteady feed to the roaster. The belt-conveyor passes through two rolls to ensure the breaking of the lumps formed in drying.

Flue losses in the dryer are small, about ten tons being collected monthly. With a sticky concentrate the dryer tends to clog, necessitating hammering occasionally with a mallet from the outside. The placing of short chains in the dryer would prevent this trouble.

The concentrate from the dryer is fed to the top, or drying hearth, of a 25-ft. 9-hearth Wedge type Skinner roaster. This roaster has a speed of approximately one revolution per minute. Mechanical trouble was practically *nil* during a year's run. For a long time it was thought that the success of the entire process lay in the roasting, and more attention was given to this than to any other operation. It was finally discovered that the roasting was not as important as believed, but that regardless of how good the roast was, unless the ore was properly cooled, results would be poor. With the right kind of cooling there is a range of temperature on which successful roasting could be ensured.

As originally built each hearth was completely bricked in, with the exception of two doors. This, it was found, made the roaster hard to regulate, and held too much heat, causing a high temperature, which oxidized the blende. The brick on the lower five hearths was removed and replaced with sheet-iron doors,

which give more radiation and facilitate control. With a Wedge, or similar iron-sheeted roaster, it would have been impossible to do this. At the same time a vertical gas-offtake was installed so that the heat and gas could be drawn from one or all hearths, permitting rapid cooling of the roaster in case of too high a temperature. This proved most useful.

No troubles being traced to the cooler and thinking that poor results at the start were due to too long a roast, it was decided to feed the concentrate on the fifth hearth. Later this was changed back to the ninth. Also, in first starting the roaster heat was applied through the muffles, but as it was necessary to put on or take off the heat quickly at times, this was not satisfactory, and the fire was applied directly to the hearths.

Under this system good results were obtained when treating only 75 tons of concentrate per day. The heat was applied on the sevénth hearth by means of oil-burners. An auxiliary burner was kept on the fifth hearth. The fuel could be turned off for days at a time, after having once heated up the furnace to the proper temperature, but it was found that a better control could be maintained with a constant light fire. On this small tonnage No. 8 and 9 hearths would be dark; No. 7 a glowing red; No. 6 a cherry-red; No. 5 a very dull red; on No. 4 the red color could just be seen; No. 3, 2, and 1 were black. Under these conditions the concentrate was receiving its oxidation on the lower hearths of the roaster, the doors of hearths No. 1, 2, 3, and 4 being wide open the greater part of the time. But there was still trouble in keeping the lower part of the hearth cool; this was finally corrected on a 75-ton basis, but when treating 150 tons of concentrate per day (the output of the concentrator) it was practically impossible to keep the lower hearths cool. The color of the roast after cooling varied from straw-yellow to black, a so-called perfect roast being of a reddish-brown color, by reason of the mixture of red oxides of copper and iron with the gray-black sphalerite.

In test-work it was found that if the concentrate was properly roasted, and left to cool gradually, the copper and iron would get the right amount of oxidation and have the character-

istic brown color, but if after roasting it was dumped on a cold bucking-board the concentrate would have a black color and when put in a flotation machine the copper and iron as well as

The Afterthought Mill

the zinc would float, the preferential action being killed entirely. Many theories were advanced as to the exact cause of this. The first was that the copper and iron in roasting had become slightly oxidized and that in chilling this film was cracked, exposing the

copper and iron sulphides. The second theory was that magnetic sulphides of iron and copper together with magnetite were formed (as the whole mass was magnetic), and that this was the cause of the concentrate floating (magnetite being more or less floatable).

After these tests had been made, samples of the roasted product were taken and cooled slowly; this gave good preferential results; so everything pointed to the fact that most of the trouble was in the cooling. The concentrate at this time was going through a 20-ft. Baker cooler, taking about three minutes to travel from the intake to the discharge. In cutting down the speed to give the concentrate a longer cooling it was found that the discharge tended to bank up. A helix was then put in, and by cutting down the speed of the cooler the concentrate was held 11 minutes. As cold water was being run into the cooler-vat, someone suggested that we " heat the cooler," and this was tried by letting the water come to a temperature of 90°, holding it at this point. The retardation of the cooling gave better results at once. A still further improvement was made by blowing air through the cooler; this tended to expel the sulphur di-oxide and gave the warm concentrate fresh air for oxidation. However, on a 150-ton basis, when the entire hearth-area had to be used for roasting and none could be used for cooling, the discharge was too hot for the cooling capacity. If the heat was held at the upper part of the roaster the concentrate discharged in a partly roasted condition. The only thing that was now needed was more cooling capacity and Mr. Milliken at once undertook to build a 120-ft. Edwards cooler. At the same time he installed an automatic recording pyrometer, which gave a record of the heat of all hearths at all times. The temperature of the hearths for obtaining good roasts should be not more than 920° F. on the hottest hearth (4th from the top) to 400°, or lower if possible, on the bottom hearth.

More or less copper sulphate was formed during roasting. When the ore was chilled there was but a trace, but with over-roasted ore the copper sulphate was at its maximum. By taking the best roasts and determining the sulphate, the proper amount

of sulphating for a good roast was obtained. Every hour it was the duty of the roaster attendant to make a colorimetric analysis of the roaster discharge. A peculiar fact about the sulphating was that the proper roast gave the right amount of sulphating for good flotation work, for it was found that, regardless of the roast, if this copper sulphate was removed the preferential results would be poor. The copper sulphate evidently helps the flotation of the zinc, besides keeping down the copper. The following is a comparative test:

Oils: 50% fuel, 50% P. T. & T. No. 80.
Ore: 40-minute dull-red roast.
Temperature flotation: 60° F.
Test No. 1. Soluble contents filtered out.
Test No. 2. Soluble contents retained.

TEST 1

	Weight, gm.	Assays.		Recoveries.	
		Cu, %	Zn, %	Cu, %	Zn, %
Copper concentrate..	167	6.80	38.2	67.2	67.4
Zinc concentrate.....	119	4.73	26.1	32.8	32.6
TEST 2					
Copper concentrate..	136	9.12	13.1	68.6	20.3
Zinc concentrate.....	157	3.62	44.6	31.4	79.7

For a long time the sulphur burnt off in roasting was as high as 50%, which meant that more or less of the blende was affected. This was soon remedied.

Under roasting, I have endeavored to give the most important of the metallurgical troubles encountered, all of which were finally overcome. What should be the proper roast it became hard to determine, because at times when it was thought that the roast was good the results were poor and the reverse was equally true. For the first few months there were times when the roaster became white-hot, then in cooling it would chill too

quickly. Again, notwithstanding the good ventilation of the roaster-building and frequent cleaning of the flues, the sulphur gas was so strong that one could hardly enter the building without a mask. The following is a set of instructions issued to the roaster attendants:

a. If for any reason roaster is stopped, have rabbles pointing in a NW-SE direction out of line of the burner flames.

b. If sulphides are burning in screw-conveyor leading to cooler or if roaster-discharge is red, it means that the heat is too low in the roaster. The heat may be brought up:

1. By increasing fires on 7th hearth.
2. By cutting down amount of feed to roaster.
3. If serious, by ringing off feed, stopping roasters for two minutes at a time and turning one revolution, wait two minutes, etc.

c. Size of fire: Do not change without authority of shift-foreman.

d. Sulphating: Color No. 2 best. Test every hour.

e. Panning-tests. Make one every hour. Compare with good roasts.

f. If panning-tests vary much from the brown color desired, report same at once to shift-foreman.

g. Look at all seals at least once on a shift.

h. Do not open or close doors without orders from shift-foreman.

i. Oiling: Line-shafting twice per shift; roaster-bearings once per shift.

j. Power off: Shut off feed and lower fires. Turn roaster once every five minutes.

k. Empty hearths denote clogged seals.

l. Do not go to top of roaster without mask or respirator.

m. Do not let level of cooling-water get below overflow.

n. Cooling-water should be steaming slightly.

Preferential Flotation.—The roaster discharge, after going through a mechanical scraper for removal of lumps, passed through the cooler and was then elevated to a conveyor running to the top of the mill, where it discharged into a sludge-tank, water being added before drawing it out to the flotation machines. Owing to the high dust-losses this method of conveying was discarded and a pumping system installed, using three lifts of 80 ft. each with two-inch Krogh sand-pumps in duplicate. Trouble was caused by the presence of copper sulphate; this was overcome to a great extent by the use of wood-stave pipe-lines and corrosion liners, with aluminum bronze impellers for the pumps. The liners were imbedded in cement. This pulp then went through seven roughing and three cleaning Janneys. Here also

sulphating caused trouble. The copper sulphate would precipitate on, and eat out, the return-pipes, liners, housings, and impellers. Calcium sulphate would also clog the mats, so that, unless prevented by pounding, the pores of the mats would be closed entirely in a week.

In February, 1918, a change was made in the design of the Janney machines by making the liners and cells entirely of wood, with spitzkasten similar in design to the mechanical Janney, but much shallower, so that there was but a foot lift from the bottom of the " spitz " to the cell. The return from the spitskasten to the cell was also made of wood. The large 45 by 45-in. iron air-pans were then cut in three pieces, each 15 by 45 in., and one placed in each spitzkasten on an angle, below the discharge from the cell. These mats could then be lifted out readily in case of a choke-up, or if the mats needed renewing. Air entered the top of the mat instead of from the bottom. The impellers were made of bronze. These machines worked so well that it was decided to install a Minerals Separation machine similar in design near the roaster, so as to avoid elevating the roasted product, at the same time giving more capacity for the collective flotation.

The reason for the installation of the Minerals Separation machine was that it was thought that there would be more ease of operation, because all the cells would be in view of the operator at one time, and the flotation of the roasted product could thus be controlled more easily. The Janneys, as remodeled in the main mill, had given excellent results when the concentrate was properly roasted, and cooled, but there was considerable expense in pumping the pulp 300 ft. to the top of the mill, and the preferential-flotation Janneys were not compact enough. By installing the M. S. machine near the roaster a better control could be had, while the Janneys could be used for collective flotation. In this particular case the Minerals Separation machine fell down, first because of the capacity of the machine and second because of the lack of agitation. The agitation given by the Janneys, even though so much greater than that obtained by the M. S. machine, was not sufficient alone to give good results on the first cells, and without some method of cleaning the zinc

particles by pumping or by emulsifiers at the head of the Janneys the best concentrate would not appear until the third or fourth cell. With the M. S. machine the only time any froth at all was formed—and then it appeared very much over-oiled, owing to lack of agitation—was when the concentrate was a little under-roasted. With this pulp under the old conditions, the Janneys could have yielded a froth that would have buried the mill. It is absolutely necessary to have a sub-aerated type of machine, in that the froth formed is slow-moving, and must be removed as soon as formed. With sufficient pre-agitation and the use of sub-aerated acid-proof Janney machines as remodeled at the Afterthought mill excellent results should be obtained with the roasted product as obtained under the conditions as finally perfected.

At first acid and heat were used in preferential work with G. N. S. No. 8 and 28 oils. After much testing, suitable oils were found giving better results and not requiring either acid or heat. Approximately 4 pounds of oil per ton of ore is used.

Flotation results varied with roasting and cooling conditions. At times there was no froth at all, and then again there was so much froth that it could not be handled. An over-roast gave a thin brittle yellowish-brown froth; an under-roast a high voluminous gray froth. A chilled roast gave a fluffy high jet-black froth, while a good roast was of a brownish-black color. Under proper conditions the zinc concentrate was gray, and the copper concentrate a brilliant red. Analysis of the products produced by preferential flotation is about as follows:

Zinc concentrate—2.6% copper, 47.1% zinc, 4.2% iron, 3.3% barite, 4.4% lime, 3.8% alumina, and 3.2% silica.

Copper concentrate—7.2% copper, 12.3% zinc, 23.4% iron, 8.2% barite, 10.7% lime, 10.5% alumina, and 10.4% silica.

There is about eight ounces of silver per ton of each concentrate. These results should be considerably improved by the new cooling system, as tests on a properly cooled ore have given as high as a 55% zinc concentrate, and a 10% copper concentrate containing but 5% zinc.

Thickening, Filtering, and Drying.—Two 16-ft. Dorr thick-

eners are provided for the zinc and copper concentrates. From each of these thickeners the pulp is drawn to one of four 6-leaf 4-ft. American filters—two for the copper and two for the zinc concentrate. The pulp to the filters contains about 25% moisture and is de-watered to 15%. The American is the only type of filter that could be used economically on these concentrates on account of the calcium sulphate present; this quickly closes the pores of the canvas. The life of the canvas filtering-bags is not more than two weeks, but the bags are cheap and can be changed by the attendant while the filters are in operation. With a drum type of filter it would be impracticable to change a cloth every ten days. From the filters the concentrate is conveyed to cylindrical dryers, of which there are two similar to the collective dryer. These dryers discharge into storage-bins. The copper concentrate is treated locally and the zinc concentrate is sent to Oklahoma.

Tailing from the collective department is partly de-watered in a 30-ft. Dorr thickener. The de-watered tailing is run to a dam modeled after the Inspiration system, placed in a canyon adjacent to the mill. The tailing-launder as it passes over the dam has 18-in. cones every ten feet, which thickens the dam-building material. The overflow from these cones settles ahead of the dam, and the water is drawn off clear in order to avoid pollution of the stream.

Costs.—Although there are not enough data available as to what the exact operating cost of the Horwood process would be on a 300-ton basis, from costs of the process obtained during the spring of 1918, the following would be a close estimate:

	Cost per ton.		Cost per ton.
Coarse crushing	$0.080	Assaying	$0.060
Sampling	0.012	Lighting and heating	0.042
Elevating and conveying	0.014	Supervision	0.120
Fine-grinding and classification	0.250	Drying	0.100
Collective flotation	0.100	General	0.130
Preferential flotation	0.150	Maintenance and buildings	0.020
Pumping	0.050	Plant and machinery repairs	0.025
Filtering	0.120	Royalty	0.500
Roasting and cooling	0.300		
Tailing-disposal	0.020	Total	$2.093

Conclusion.—Considering how little was known concerning the Horwood process as applied to a copper-iron-zinc ore, rapid progress has been made with this system at the Afterthought mine. The plant ran intermittently for over a year, and shutdowns were only made to improve the practice and install machinery, until the drop in price of the metals and development of the electrolytic process showed that this latter process would be best on this ore. With a high power-rate, which would make the electrolytic method out of the question, or with a cheaper freight-rate and higher metal-prices, undoubtedly the Horwood process as developed at the Afterthought mine would be best suited to this ore.

The flow-sheet now has the same outline as when the plant was first started. The most important improvements made were in the kind and cost of reagents; the steady regulation of the roaster for a low temperature; the removal of lumps from the feed to the roaster and from the feed to preferential flotation; a change in the method of cooling; and in the position of the preferential plant; the drying of the copper and zinc concentrates, and the local treatment of the copper concentrate.

The field for the Horwood process today is limited, since on ores upon which fairly good results may be obtained by gravity or gravity and flotation methods the Horwood process could not compete. The same is true of a complex ore where the electrolytic process is practicable. Notwithstanding recent developments of the Bradford and allied processes, and the higher initial and operating costs of the Horwood, there is no doubt that the Horwood process will give better results in some cases than can be expected with the wet preferential methods.

A MODIFICATION OF HORWOOD'S PROCESS FOR THE TREATMENT OF COPPER-ZINC ORES [1]

By H. L. Hazen

The separation of the sulphides of copper from sphalerite is a metallurgical problem that has been solved successfully in comparatively few instances. Perhaps the main reason for the lack of success has been the difficulty in maintaining constant the conditions found necessary for the production of a high-grade zinc concentrate containing little copper and a copper concentrate sufficiently low in zinc to escape the penalty imposed by the purchasing smelter. Preferential-flotation methods still hold out a promise, but most of these methods require a delicate control of conditions that is difficult to maintain in a mill. Another method that has received considerable attention is Horwood's which was evolved for the separation of lead sulphide from the sulphide of zinc.

As is well known, Horwood's method consists essentially of:

First. Extraction of the sulphides from the ore in a mixed concentrate.

Second. Giving the concentrate a quick roast at a temperature ranging from 300° to 500° C. for the purpose of forming an oxide film on all the minerals except the sulphide of zinc.

Third. Re-treatment of the roasted material by flotation, the sphalerite concentrating out in a high-grade product, leaving the major portion of the other minerals in the tailing.

When applied to copper-zinc ores this method has been successful for short periods of time, a high-grade zinc concentrate and a copper concentrate low in zinc being obtained. In continuous operations, however, it has not been found possible to keep constant the required temperature in the roasting operation and the resultant flotation products could not be marketed. To illustrate: if the temperature in the furnace became too high

[1] From the *Mining and Scientific Press* of March 27, 1920.

the sulphide of zinc was superficially oxidized and would not respond to the subsequent flotation treatment. If sulphuric acid was used to dissolve this zinc oxide off the sphalerite prior to flotation, the acid also cleaned the copper sulphides, after which flotation gave a copper-zinc concentrate and the millman was no better off than he was before the roast.

For the purpose of eliminating the necessity for accurate and careful control of the roasting conditions and in order always to be certain of obtaining a copper concentrate sufficiently low in zinc to escape penalty and a high-grade zinc concentrate, the following modification of Horwood's method is suggested:

First. Concentrate the ore into a mixed concentrate of all the desired minerals.

Second. Roast this bulk concentrate at a temperature in excess of 300° C. for a sufficient time to oxidize completely the copper sulphides.

Third. Transfer the roasted material to suitable equipment and dissolve out the copper sulphate formed during the roast with water sufficiently acidulated with sulphuric acid to remove whatever zinc oxide has formed on the sphalerite. The copper can be readily recovered from solution by precipitation on iron.

Fourth. Treat the residue by flotation for the purpose of extracting the sphalerite in a high-grade zinc concentrate. The flotation tailing will be a concentrate of copper containing little zinc.

The basis for this suggestion is a number of tests made on various complex base-metal ores. In every case the test was carried out in the same manner and the results obtained with each ore were so similar that the details of two of the tests made on ores from different localities will be sufficient to illustrate the results that could be expected from this treatment.

Sufficient ore was concentrated by flotation to give a mixed concentrate weighing 500 grams. This concentrate was then placed in a roasting-dish in a muffle, which was heated until the copper sulphides were well ignited, the temperature reached being 300° C. All external heat was then removed from under the muffle and the concentrate, which was self-combustible,

allowed to burn freely in a good supply of air and rabbled frequently. The temperature of the roast rose rapidly to a maximum of 470° and maintained itself there for about an hour, after which it fell gradually as the combustion neared completion. The calcine was agitated for 30 minutes with water acidulated with four pounds of sulphuric acid per ton of calcine, the pulp filtered and the dissolved copper recovered from the effluent by precipitation on scrap-iron. The residue was transferred to a flotation machine and the sphalerite concentrated out, leaving a tailing commercially free of zinc.

The results of these tests are shown in the accompanying data. See Table 1.

TABLE 1.—DETAILS OF TEST MADE ON FIRST SAMPLE OF ORE

Product.	Weight, %	Assay.					
		Au, $	Ag, oz.	Cu, %	Pb, %	Zn, %	Fe, %
Original ore	100.00	5.61	2.17	2.24	0.45	11.88	19.38
Bulk-flotation concentrate	60.20	5.58	2.94	2.96	0.80	18.66	27.45
Flotation zinc concentrate after roast	18.51	7.03	4.26	1.34	0.30	54.48	4.74
Flotation middling after roast	4.66	19.02	8.36	4.47	3.45	10.50	21.71
Flotation tailing after roast (copper concentrate)	21.98	5.37	2.70	2.92	1.20	0.92	60.60
In solution	.....	.....	.....	.....	.....	.....	.....

Product.	Weight, %	Distribution.					
		Au, %	Ag, %	Cu, %	Pb, %	Zn, %	Fe, %
Original ore	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Bulk-flotation concentrate	60.20	60.90	90.77	96.74	100.00	97.67	94.08
Flotation zinc concentrate after roast	18.51	23.68	40.51	13.57	10.64	87.65	5.01
Flotation middling after roast	4.66	16.16	20.00	11.41	34.04	4.26	5.75
Flotation tailing after roast (copper concentrate)	21.98	21.43	30.26	34.78	55.86	1.74	75.80
In solution	.....	none	none	37.50	none	4.00	7.52

As shown in the preceding table, 37.50% of the copper content of the ore was recovered as cement copper and 46.20% more obtained in a product sufficiently low in zinc to escape penalty by a smelter, making a total extraction of 83.7% of the copper in the ore. The zinc concentrate assayed 54.4% zinc and contained 87.6% of the zinc in the ore.

As a matter of interest it may be stated that another test made on the calcine showed that 80% of the copper in the ore could have been dissolved had sufficient acid been used after the roast. It will be noticed that the copper concentrate, after the flotation of the zinc, assayed slightly less than 3% copper, but under the marketing conditions peculiar to this ore it was decided that a larger profit could be made by marketing this product direct than by dissolving out the copper with acid and selling cement copper.

The results obtained in this test could have been improved both by better control in the first flotation treatment (for instance, most of the iron could have been dropped out without serious loss in the copper extraction) and by better control of the subsequent roast, as the amount of zinc oxidized and subsequently lost in solution depends upon the temperature of the roast.

TABLE 2.—DETAILS OF TEST MADE ON SECOND SAMPLE OF ORE

Product.	Weight, %	Assay.		Distribution.	
		Cu, %	Zn, %	Cu, %	Zn, %
Original ore	100.00	3.11	10.79	100.00	100.00
Bulk-flotation concentration	48.76	6.03	20.77	94.64	94.88
Flotation zinc concentrate after roast	10.56	1.68	55.81	5.79	54.59
Flotation middling after roast	6.98	5.11	36.19	11.58	23.45
Flotation tailing after roast (copper concentrate)	19.53	6.39	4.28	40.19	7.78
In solution	.....	.....	.....	37.62	8.53

It is seen in the above table that 37.6% of the copper in the ore was recovered as cement copper and 40.1% more obtained

in a product low in zinc, making a total extraction of 77.7% of the copper. The zinc concentrate assayed 55.8% zinc and contained 54.6% of the zinc in the ore. In addition, a further recovery of copper concentrate and zinc concentrate would be obtained from the middling when it returned, in the normal course of milling, to the roughing-cells for re-treatment.

Probably the most serious objection to this method would be the loss of dissolved zinc, and the higher the temperature reached in the roast the greater would be the amount of zinc oxidized and dissolved from the calcine. The extraction of a portion of the copper as sulphate in solution might or might not be a drawback on account of the cost of the operation, and this would depend upon whether the zinc tailing is to be marketed as a copper concentrate or whether it would be preferable in the circumstances to dissolve out the maximum possible amount of copper with acid and market it as cement copper.

The great advantage that it is believed this modified treatment would have over Horwood's method in the concentration of copper-zinc ores is that no great delicacy of control would be needed for the production of a high-grade zinc concentrate and a salable copper product. No matter to what temperature the roast should be taken, a day's run would not be spoiled by a zinky copper concentrate: it would merely mean that more acid must be used to clean the sphalerite and that more zinc would be lost in solution, but the copper and zinc concentrates would remain of a uniform grade.

FLOTATION PRACTICE OF THE UTAH COPPER COMPANY [1]

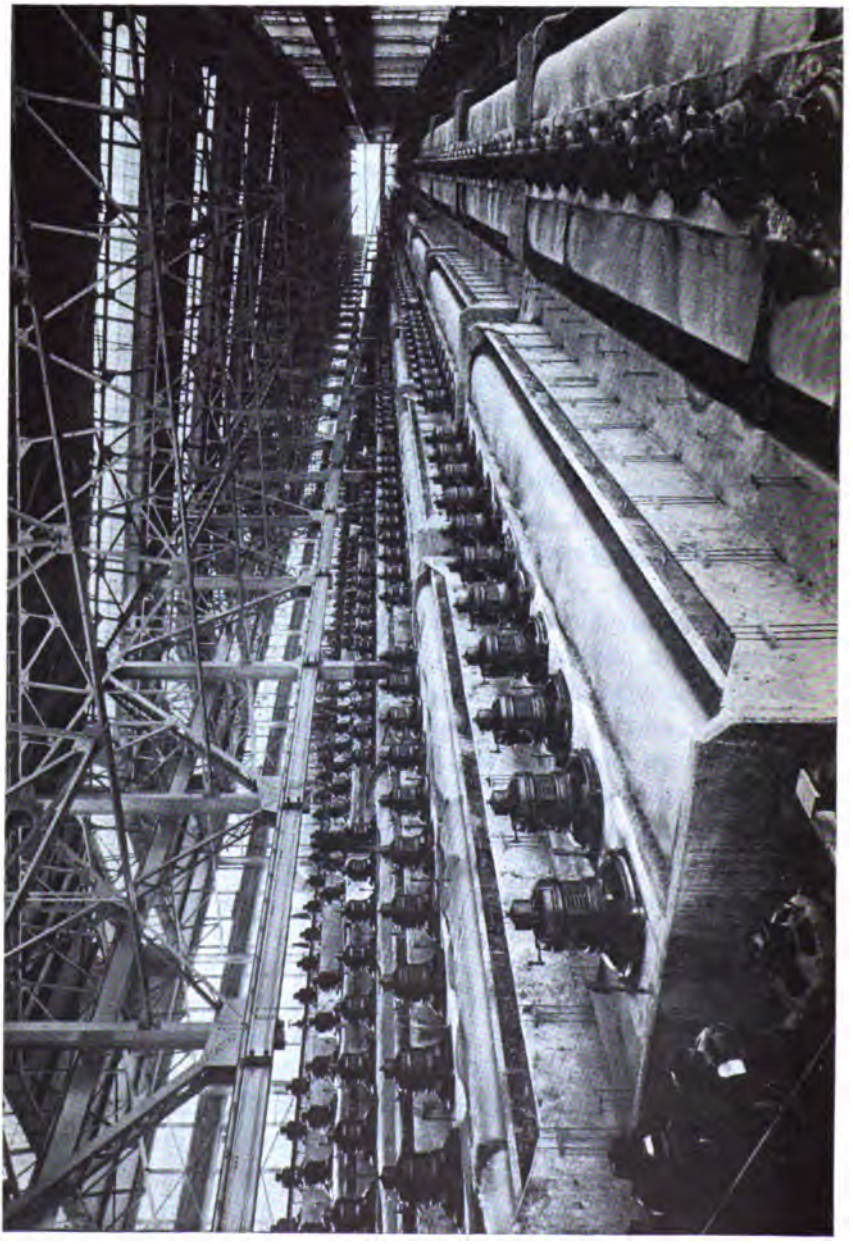
By T. A. Rickard

Treatment of Vanner Concentrate.—This goes first to two 44 by 20-ft. Dorr thickeners, which increase the density of the feed from 6 to 24. The thickened product passes to two emulsifiers and 13 Janney cells of the mechanical type. They are placed in series, stepping six inches. All that is visible of this machine is the hood, which contains the motor. The vent-holes for the field-cores make it look like a beehive, the emblem of Utah.

This machine for froth-flotation was designed by T. A. Janney at the Arthur mill, and is the result of systematic experimental work in which the inventor was assisted by his late father, Frank G. Janney, and his brother, Frank G. Janney, Jr. Two types of machine have been developed. One is the "mechanical," this term being used to designate the kind of agitation it produces, in contradistinction to the other type, which is based upon the pneumatic, as well as the mechanical principle.

The "mechanical" Janney consists of a chamber (22 in. diam. by 26 in. high) in which revolves a shaft carrying two impellers, each having four blades set at an angle of 45° and revolving at 570 r.p.m. This stirrer is actuated by an electric motor, to which the shaft is directly connected. When ready for work the hood containing the motor is the only part of the machine that is visible. Four baffles are fixed around the periphery of the chamber, the lower impeller moving inside these baffles on a level about one inch from the bottom, while the upper impeller moves one inch above the baffles, the effect being to

[1] From the *Mining and Scientific Press* of December 7, 1918.



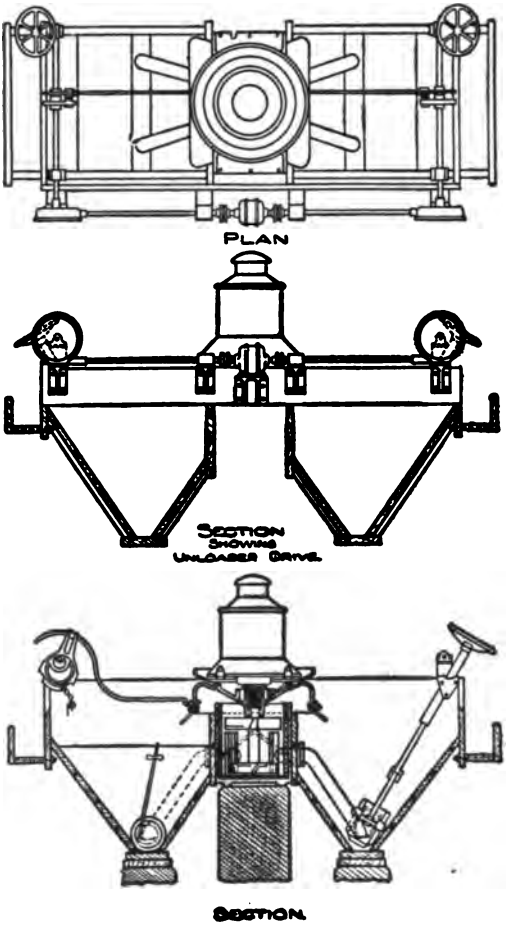
The Janney Flotation Machines in the Arthur Mill.

ensure a complete and violent agitation of the pulp. Besides stirring the pulp, the impellers induce a circulation from the chamber to the spitzkasten and return. The spitzkasten, a V-shaped base attached to each side of the principal mechanism, receives the pulp after it has undergone such stirring as will create the froth essential to the process. The froth rises to the surface of the pulp in the spitzkasten and is skimmed into a launder. The skimmer consists of a blade attached to an interrupted eccentric that while revolving drops the blade into the froth so as to give first a vertical and then a horizontal motion, thereby avoiding the breaking of the froth. The amplitude of the sweep of this skimmer is regulated by the throw of the eccentric; the depth of the skimming is controlled by a bent rod to which the eccentric is attached and by which it is maintained in the desired position. An important feature of the invention is the circulation of the pulp. The feed enters through a gate at the bottom of the " spitz " and is drawn, by displacement, into a pipe that takes it directly to the agitating-chamber; it is then thrown upward and outward near the top of the " spitz." Thus a constant circulation is maintained, the volume of pulp undergoing treatment being five or six times as much as the volume of feed or of discharge.

The " mechanical-air " machine, as it is called, has the same kind of agitating-chamber, but the spitzkasten is provided with a porous bottom inclined at an angle of 35°. This porous bottom, or " air-mat," is made of four plies of canvas through which air under a pressure of $3\frac{1}{2}$ to 5 pounds is admitted. The air-pan is divided into three compartments, fed from corresponding pipes. The division is intended to compensate for the varying hydraulic head, thereby ensuring a uniform admission of air into the pulp.

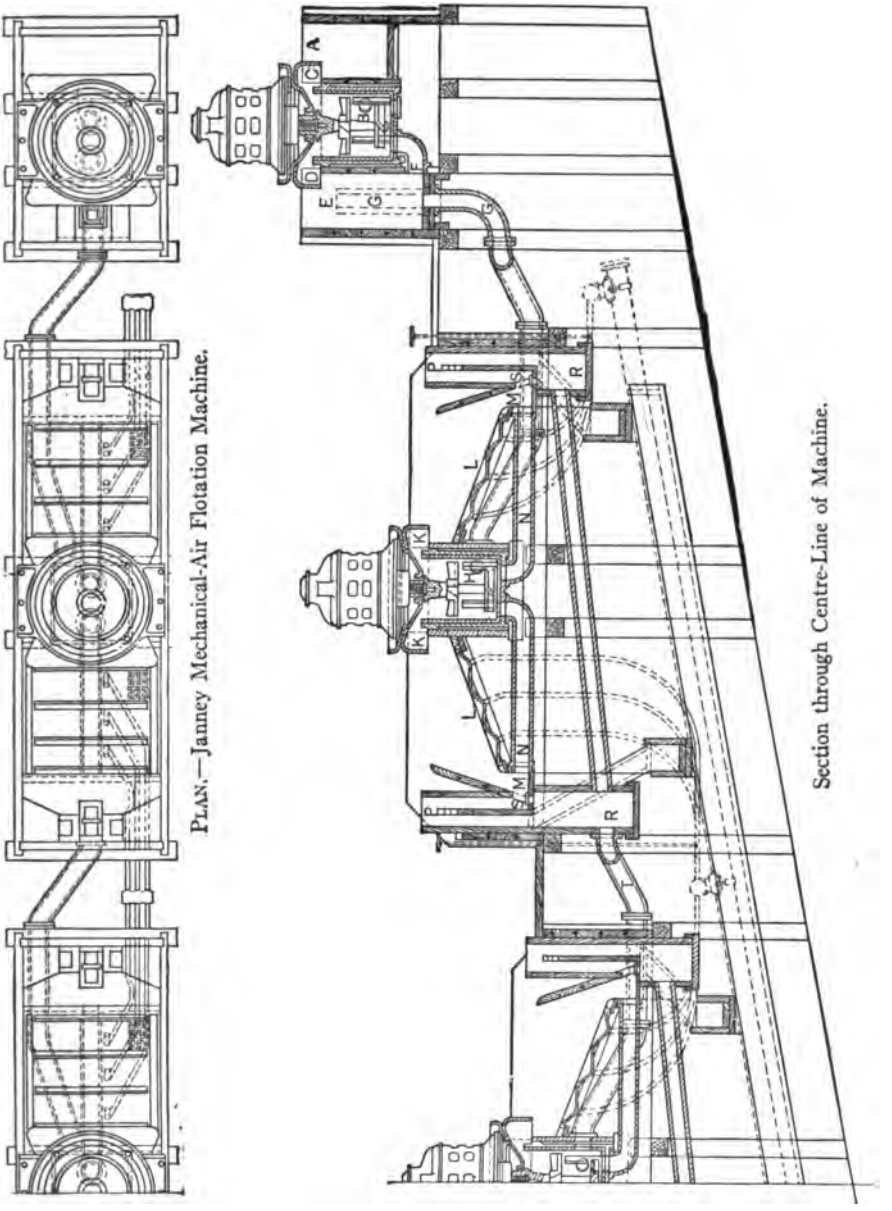
The first machine in a series of either type of Janney equipment is used as a preliminary mixer, or " emulsifier." At this stage no metallurgical product is forthcoming. Here oil or other modifying agents are added just before the feed enters the mixer, and the pulp is prepared for the actual froth-making that follows in the second machine of the series, whatever the number of machines. The oil is added by means of a special device, de-

signed to secure the constant feed necessary for the operations that are to follow.



JANNEY MECHANICAL FLOTATION MACHINE.

From this mixer, or " emulsifier," the pulp enters the " mechanical-air " machine at the side of the agitating-chamber



PLAN.—Janney Mechanical-Air Flotation Machine.

Section through Centre-Line of Machine.

(above the lower impeller); thence it is ejected into the spitzkasten at a level higher than the inlet. In this chamber, which is open under the motor, there is an indrawing of air, as shown by a lighted match. In the " spitz " the further aeration of the pulp is effected by the air that enters through the porous bottom, causing bubbles to be generated freely in the pulp, so as to buoy the particles of mineral to the surface.

The froth produced by the two types of machines differs notably, that of the " mechanical " being denser and tougher than the froth in the " mechanical-air," the product of which is more readily broken after it has been discharged, because, of course, once the froth has done its duty, it becomes a nuisance. The sooner it differentiates into liquid and solid the better. The reject of this operation descends over the air-mat to be returned by an interior pipe from each " spitz " back to the agitating-chamber, the excess escaping over a weir into a launder or pipe that takes it to the next machine in the series. The froth from the " roughing " machines is re-treated in the " cleaners," to which it is pumped. The tailing from the " cleaners " is pumped back and rejoins the feed to the " roughers." On the other hand, the reject from the " mechanical " Janney goes direct to waste.

Turning to the drawing of the " mechanical-air " machine, let us follow the flow of the pulp. It is fed at *A* and enters the opening *B*, part of it being thrown out at *C*, to rejoin *A*, producing a half-circulation at this stage. The other half is ejected at *D*, where the pulp drops into the box *E*, from which a portion is again drawn into the mixing-chamber through the pipe *F*, producing the other half of the circulation. The excess, equal to the feed, escapes through the pipe *G* into the next machine, which it enters at *H*, where it is ejected, at the points *KK*, into the spitzkasten, passing over the air-mats *LL* to the box at *M*, where part of the pulp passes back through the pipe *N*, joining the original feed of this machine at *OO*, while the excess escapes at *M*, the sand dropping through the spigot *S*, while the slime rises over the weir *P* and falls into the box, where it joins the sand, the joint products passing through *T* into the next machine.

Returning to the flotation of the vanner-concentrate; a sample of the froth when shaken in a pan and patted with the hand, so as to break the bubbles, shows the black copper sulphide that has settled underneath. The first six cells produce a concentrate containing 25% copper, 21% iron, and 20% insoluble. The number of cells in use to produce a finished product is regulated by the character of the feed, any cell being made to yield either a middling or a concentrate by shifting the baffle that divides the launder lengthwise into two compartments. The product of the last seven cells is a middling, which is returned for re-treatment.

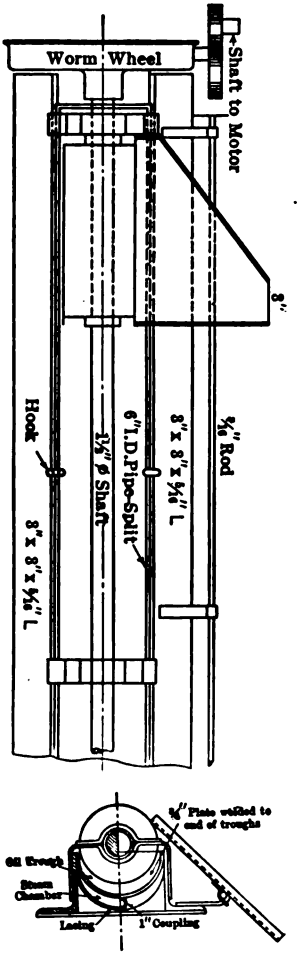
The oil-mixture consists of mineral, pine, and creosote oils. The feeding of the oil is effected by a special machine of water-wheel type; it is a wheel having small buckets on its periphery dipping into a tank of oil that is kept at a constant level by a constant inflow, the excess returning to a storage-tank, to be returned by a centrifugal pump. The tank to which it returns is equipped with a steam-coil so as to maintain the oil at a uniform consistence. The speed of the feed-wheel is controlled by a friction-disc that regulates the speed as required, maintaining the feed of oil in excess of 10 lb. per ton of ore. A sulphonated alkali, called " calura," is added to the pulp before it enters the two emulsifiers in order to act, like acid, as an electrolyte; and thereby increase the efficiency of the process, it having been found that the feed requires an alkali instead of an acid. The slimed feed requires an acid; the granular feed an alkali. The amount of vanner-concentrate sent to flotation is 466 tons daily; that of slime is 12,000 tons.

Treatment of Slime.—The slime from the water-concentrating mill runs into ten Dorr thickeners, six of which are 75 by 12 ft. and four 75 by 18 ft. Four more, 75 by 18 ft., are being added. The density of the inflow is 8, and the density of the outflow 24.

From the thickeners the pulp passes to three small equalizing-tanks (8 by 12 ft.). Eventually six equalizers will serve 14 thickeners. The purpose is to correct any fluctuation of feed to the flotation machines, and also to mix the feed with the middling that is returned from the cleaner-cells of the flotation de-

partment. Acid is added to the equalizers at the rate of three pounds of 60° B. sulphuric acid per ton of ore.

From the equalizers the pulp is conducted through 12-in. wooden pipes into a 24-in. concrete pipe that extends the entire width, 583 ft., of the flotation plant. From this conduit the pulp is distributed by 4-in. pipe to each row of cells—each row consisting of one emulsifier and five cells. There are 11 such rows to each unit of the plant, which when complete will consist of 11 units, 8 of them roughers and 2 cleaners, and one a re-cleaner. Thus there are 726 machines, of which 605 are working-cells and 121 emulsifiers. The emulsifier serves to distribute the oil equally throughout the pulp before it enters the working-cell.



Oil-Feeding Device

In the roughing-cell a low-grade concentrate is produced and a clean tailing, the concentrate itself being re-treated in the "cleaner," while the tailing goes to waste. The tailing from the cleaner is returned to equalizing-tanks, in which it is mixed with fresh feed. The oil, at the rate of more than 10 lb. per ton of ore, is added by means of a special feeder, which consists of a flat-faced pulley that dips into a small tank of oil and thereby collects a film, to be removed by a scraper impinging on the face of the pulley just above the point where it enters the oil. This feeder is adjustable by the width of the overlap of the scraper.

No skimming device is used in the air-cells. The froth rises

sufficiently fast, owing to the large volume of air forced through the porous bottom, to push the mineral-laden froth over the edge of the cell.

The air-machine in use at the time of my visit consisted of five twin-cells, back to back. This entire plant was made of concrete and tile, the latter for piping. Each cell was 9 ft. 4 in. by 4 ft. 3 in. The porous medium was a four-ply canvas stretched crosswise doubly on half-inch centres. Experiments were being made with concrete mats, because the canvas wore out after being in use for eight weeks. Air was admitted at the rate of 150 cubic feet per minute under 4½ lb. pressure. No air-machines are now in use.

The low-grade concentrate from the roughers is returned to two equalizing-tanks, 20 ft. diam. by 30 ft. high, from which it flows into a 24-in. concrete pipe and is distributed to each cleaner-cell through a 4-in. pipe made of concrete and tile. No oil is added to the cleaner, only to the cleaner-tailing before it is returned to the roughing-cell. The mixing of the oil for the mechanical-air machines is done by the emulsifier, the oil being added through valves on a 6-in. header, or pipe, through which runs a steam-pipe, maintaining the oil at a uniform consistence, the oil running from this pipe through ½-in. globe-valves directly to the emulsifier. On account of the large quantity of oil used it is not necessary to employ a mechanical feeder, the volume of oil sufficing to induce a continuous flow that is readily controlled by the valve.

The composition of concentrate and of tailing is as follows:

	Per Cent.
Concentrate:	
Copper	18
Iron	17
Insoluble	34
Tailing:	
Copper	0.25

From five units the products run into wooden launders; from three units the rougher product and tailing, as well as the cleaner-tailing, drop in a cascade directly into separate concrete launders, the tailing-launder being 6 ft. wide and the concentrate-launder

10 ft. 6 in. wide. These deliver their contents to the return-pumps and main tailing-launders are required. The effect is to produce a small metallurgical Niagara, the function of which is to break the bubbles and produce a product more readily pumped.

At the far end of the annex, looking down over a series of five double-cells, there is visible a big surface of froth—a veritable boiling sea—the five units occupying a space 100 by 265 feet.

Looking at a series of machines one can note differences in the froth due to causes recognized by the experienced millman. The best type of froth consists of light-gray bubbles, fairly large (two or three inches), of an evanescent character, that is, they burst as soon as they have done their duty of buoying the valuable mineral. A bad froth is lighter in color, the bubbles smaller, and not bursting sufficiently soon. Here I may mention that manipulation is an important factor in flotation. Much of it is empirical rather than scientific, it is not patentable nor is it well adapted to description, therefore the importance of it has not been emphasized either in litigation or in technical literature, but it has played and will continue to play a decisive part in successful flotation.

The two kinds of froth-concentrate are conducted by concrete launders to elevators that discharge into Dorr thickening-tanks, 75 ft. diam. by 20 ft. high, of which seven are in operation and one is being constructed. Here the density is increased from 9 to 51. These tanks are operated in pairs and in series, also intermittently, the idea being to operate a pair until the overflow from the second tank indicates that the suspended solid has accumulated to a level near the discharge, then the feed is diverted to another pair of tanks, until the same stage of repletion is reached. Experience shows that these tanks cannot be used as efficiently in parallel continuously as in series intermittently, because the range of the settling-rate is so great in the froth-concentrate that the colloids accumulate and remain in suspension within the tank.

Filtration.—The concentrate produced by water, in the upper mill, flows in concrete launders to four drag-classifiers, which yield two products: (1) the slime, which carries the bulk of the water and flows to a bucket-elevator and is raised to a Dorr thick-

ener (75 ft. diam. by 20 ft. high), the seventh tank of this kind; (2) the coarse portion, which contains about 10% moisture, is discharged upon a belt-conveyor (leading to elevators) that unites this product with the thickened flotation product coming from the other Dorr thickeners. Thus the water-concentrate is mixed with the froth-concentrate before undergoing filtration.

The filter-plant consists of eleven 14 by 14-ft. Portland filters. Another is to be added shortly. Of these 8 to 11 are in constant use. They consist of revolving drums on which a porous medium of canvas is stretched; this is immersed in the concentrate during a part of its revolution, the pulp being drawn to the canvas by the vacuum induced within the drum. The pulp is sucked, and becoming de-watered, is detached by compressed air, which replaces the vacuum. Three Ingersoll-Rand vacuum-pumps of 9900 cu. ft. capacity per minute serve to operate the filters, which make one revolution every 15 minutes. The vacuum capacity is equal to 1.5 cu. ft. of displacement per square foot of filtering area. The filter-cloth is No. 3 Oakdale canvas. Live steam is injected at the bottom of the hopper in order to heat the pulp and also to agitate it, keeping the coarse particles in suspension. These filters are not equipped with any mechanical device for producing agitation, because experience has shown that no agitation is required other than that caused by the introduction of the steam, as described. The hotter the pulp, the dryer the cake. As the vacuum withdraws the moisture the pulp forms a cake that is loosened by compressed air and removed from the surface of the revolving drum by a scraper riding on the wires that wrap the filter. The scraper consists of steel plates, which warp and have to be replaced frequently. Experiments are being made with a scraper made in sections, so as to allow closer and more frequent adjustment, and thereby induce a clean removal of the cake.

From the filter the concentrate drops upon a belt-conveyor leading to a short inclined conveyor that discharges directly into a railroad-car. One man, with a hoe, is employed to supervise the loading. Five men are employed in the filter-plant per shift.

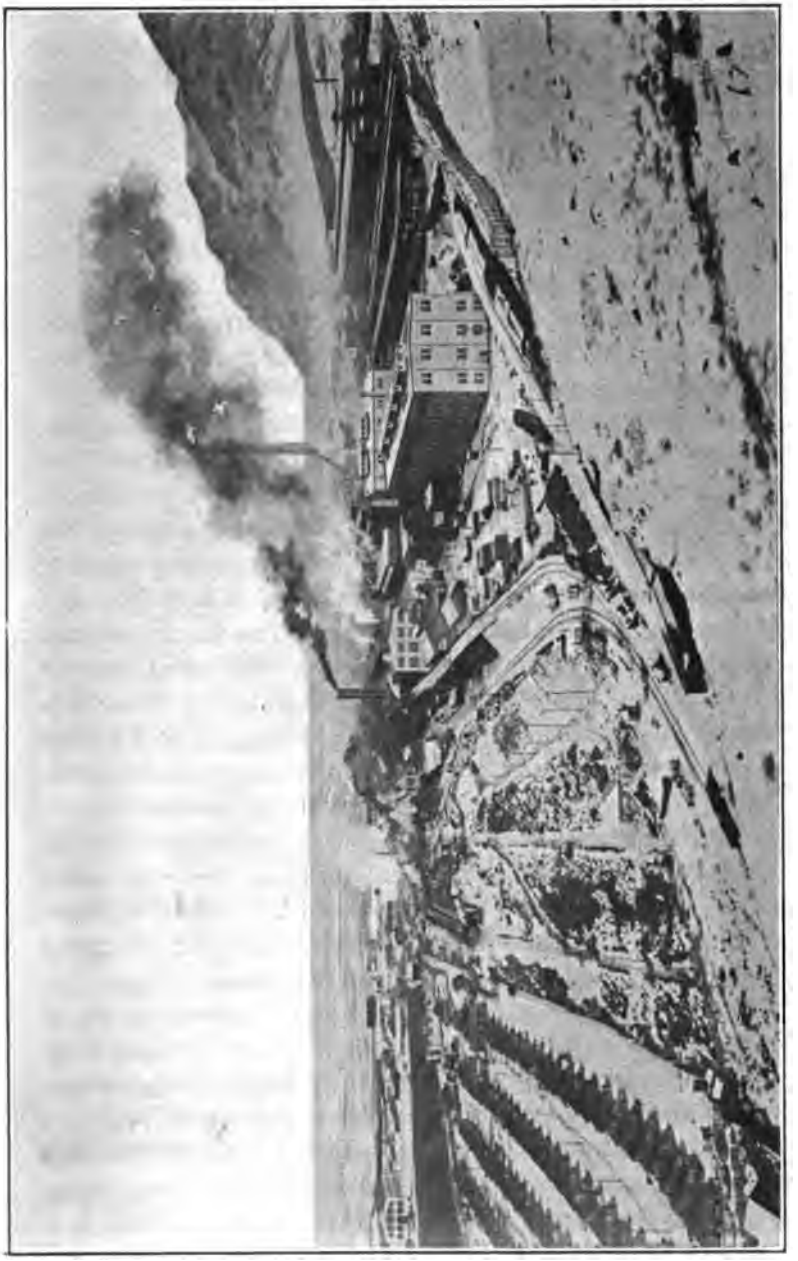
THE SMELTING OF FLOTATION CONCENTRATE AT GARFIELD [1]

By T. A. Rickard

The products of the Arthur mill, as we have seen, consist of two kinds of concentrate, one made by water and the other made by flotation. These concentrates are mixed before being delivered to the filter-plant, so that the final output of the mill is a product containing, on average, during 1917 for example, 14.82% copper, 26.79% iron, and 21.69% insoluble, together with 13.6% moisture. The last item is of greatest importance to the smelter, as we shall see. Formerly the table concentrate and the flotation concentrate were shipped separately, the first containing about 8% and the second from 20 to 25% moisture. They used to be loaded into the cars together, not properly mixed, the consequence being that accurate sampling was rendered impracticable, for the flotation concentrate was much richer in copper, containing 20% as against 12% in the table concentrate. So it was decided to ship these products separately, in order to facilitate sampling, but the cars containing the flotation concentrate had to be left on a siding for a week or more in order to allow the water to drain. Finally the management at the mill devised the scheme of mixing the table concentrate with the flotation concentrate in the Dorr thickener before filtering, thereby yielding a product containing 16 to 17% moisture. This was material that, it was thought, could be sampled fairly well.

However, before discussing this tender subject further, let us go to the Garfield smelter, to which the concentrate from the Arthur mill is consigned under contract. This smelter belongs to the American Smelting & Refining Co., it is only two miles from

[1] From the *Mining and Scientific Press* of December 28, 1918.



The Garfield Smelter of the American Smelting & Refining Co., at Garfield, Utah.

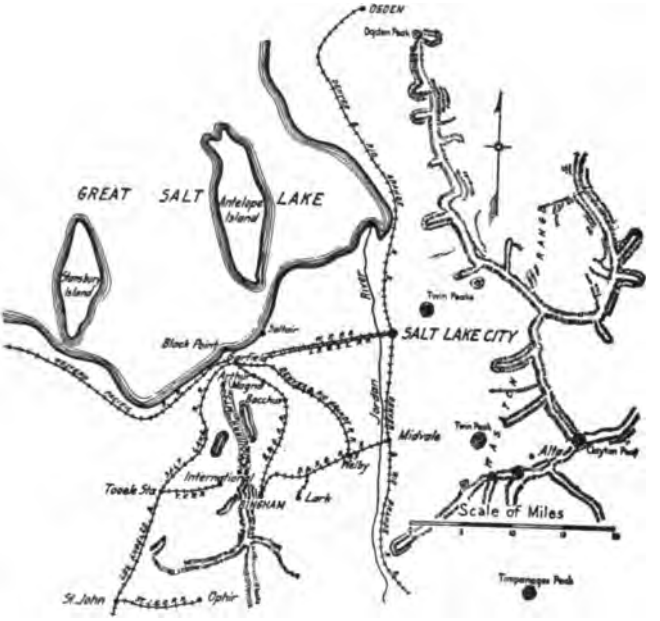
the Arthur mill, and stands on the shore of Salt Lake, near Black Rock point. The Garfield smelter treats only custom ores. At the present time 60% of the gross tonnage of ores comes from the Utah Copper company. Only a small proportion of precious-metal ore, averaging 10 oz. silver, is included in the receipts, the richest containing 32 oz. silver per ton and being used in the converter owing to its high content of silica. The 24.6% insoluble in the flotation concentrate from the Utah Copper contains 6.7% alumina and 16.9% silica.

The manager of the plant, R. F. McElvenny, was most courteous, and A. H. Richards, the assistant-superintendent, was kind enough to conduct me through the works.

A car of flotation concentrate from the Ohio Copper company was being unloaded. It contained about 25% moisture, and while watching the shoveling one could realize what trouble the Utah Copper product used to give to the smelter people. The flotation concentrate arrives in flat-bottom cars having a floor of wooden slats on which cocoa matting is spread so as to serve as a filter through which the water can drain. The car arrives with a pool of water on top; in winter this takes the form of a cake of ice two or three inches thick. From November to March it is customary to run the cars into a thawing-house. This is a brick building provided with four tracks giving room for 12 cars apiece, so that 48 cars can be thawed concurrently. In this building is a pit covered with cast-iron (one inch thick), under which is a big brick flue through which hot air passes from a furnace fired with coal. A temperature of 110° is maintained. Usually 24 hours suffices to thaw the concentrate, but if it is frozen solid, the period of thawing may be lengthened to two whole days.

The unloading is performed under contract with gangs of Greeks, also a few Japanese. These men expect to earn from $6 to $7 per day, for they work hard. The price for unloading concentrates from the Utah Copper mills varies with the moisture; for table concentrate it is $9.60; for mixed table and flotation concentrates it is $11.50; and for straight flotation concentrate, $13.35 per railroad-car. The price of $11.50 for the mixed product was maintained only during a short period, because this

material was so sticky, the unloaders insisting that it was as bad as the unmixed flotation concentrate, so that recently $13.35 has been paid for unloading the mixed concentrates. Since my visit a general rise in wages has lifted the contract prices to $10.60, $12.50, and $14.35 for the three classes of material; and, as a matter of fact, it has been found necessary to pay $14.35 on all the concentrates. A car holds 70 tons and the crew that does the



Map of part of Utah, showing the position of Garfield, also the Magna and Arthur Mills.

shoveling consists of 8 men. The price is determined by agreement before the job is tackled. In order to ascertain the proportion of moisture, holes are dug into the concentrate at two points, each one-third of the distance between the centre and the ends of the car. Both holes are dug right down to the bottom of the car and a sample is taken from each hole by means of a spoon or scoop, which is an inch wide, three inches long, and is provided with vertical sides that give a depth of one inch. In taking this moisture-sample a uniform slot is cut on the face of

the hole from the top of the load of concentrate to the very bottom of the car. While visiting the unloading-shed, above the receiving-bins, I found that a gang of shovelers had struck, demanding $13.35 for unloading a car of Utah Copper concentrate that happened to be unusually wet. It was, they claimed, a load of flotation concentrate unmixed with table concentrate. These men knew the difference. They stopped work, but the difficulty was adjusted later.

Every tenth shovel from the railroad-car is thrown onto a platform where it is half-shoveled twice, one quarter being shoveled into a car that delivers it at the sampling-room. From a small bin it is drawn onto a steel floor, upon which it is reduced by successive quartering to a sample of 200 pounds. The operator throws every other shovelful into a wheelbarrow in order to decrease the labor involved, the stickiness of the concentrate rendering it impracticable to make a regular cone. He simply shovels toward the centre, makes a heap, and then flattens the mass, using an iron sector to mark the quarters.

From the receiving-bins the ore is conveyed on a belt to the bedding-bins, whence it is discharged into lorries. Each of the four bins is 20 ft. wide and holds 7200 tons, occupying a building that is 80 ft. wide by 540 ft. long. The discharge is done by using a pick to move the boards on the bottom of the bin, which are made hopper-bottom by allowing the ore to collect at the sides. Five men are employed to empty the bin and load the lorry.

A 10% addition of silicious oxidized ore, containing 50% SiO_2, is added to the concentrate in these bins. Lime, in the proportion of 10%, is added on the fifth hearth of the roasting-furnace, so as to obtain an intimate mixture. The lime used at this smelter is in the form of sand from the shore of the big lake, a deposit of it having been discovered and first used by W. H. Howard in 1909. It contains 48% CaO and 9% insoluble.

In approaching the roaster I heard a noise that furnished further evidence of the difficulties made by the millman for the smelter. Three men were engaged in hammering the lorry, one poking with a crowbar from above, while two were hitting the

sides with a special implement, namely a bar having a knob at each end. Thus even in summer the stickiness of the concentrate

Unloading Flotation Concentrate at the Garfield Smelter.

gives this further trouble. In winter the difficulty of unloading the electric lorry is increased, of course. It appeared a pathetic performance in this age of proud efficiency, but I confess that by

this time my sympathy had veered to the smelter-people, who, it seemed to me, were called upon to overcome difficulties that had been passed to them from the mill. Mr. Richards informed me that his operations were curtailed frequently, especially during winter, by the inability to get the concentrate out of the railroad-cars and then by the difficulty of feeding it to the roasters; even after it has been mixed with 10% of silicious ore, it is difficult to ensure a uniform feed to the furnace. This is true of operations during the winter, but in summer also there is trouble in feeding concentrate to the roasters. In a recent letter from Mr. Richards he says: " I was over to the roasters this morning and found that the product we are now receiving is ' bridging ' in the hoppers of the Call-Wagstaff furnaces. You will recall that this set of roasters has the apron-feeder underneath. I counted no less than 12 men poking the charge out of the hoppers, so as to get it into the roasters, and even at that our reverberatories were curtailed owing to not being able to obtain sufficient calcine." No metallurgist can refuse his sympathy to a superintendent compelled to roast undried flotation concentrate.

New cars are to replace the lorries now in use; three of them will constitute the train to be pulled by the electric locomotive; they will carry 20 tons divided in two compartments, having vertical sides, so that when the bottom drops the load will fall promptly.

Of the various feeders, the Stevens-Adamson apron appears to work best on wet material. This feeder has a storage-hopper, two sides of which are vertical, whereas the other two slope at 70°. A 40-in. belt of overlapping corrugated steel slats 4 in. wide moves the ore, the flow of which is regulated by a gate, giving an opening 12 in. high and 36 in. wide. I saw what an inefficient feeder, of another type, will do. The concentrate stuck so as to bridge the opening and stop the feeding.

The roasters at Garfield are of the McDougall type, with rabbles having straight blades set at 45°, except on the top hearth, where the angle is 60°. The blades have a 3-in. sweep and are 6 in. apart. In order to prevent clogging by the flotation concentrate, it is proposed to widen the blades from 7 in. to 11 in. on

the topmost hearth, where four arms with rabbles spaced 9 in. apart are in use. The roasting-plant contains 48 furnaces, divided as follows:

10 Herreshoff furnaces, with seven hearths of 19½ ft. diameter.

8 Call-Wagstaff furnaces, with eight hearths, also 19½ ft. diameter. This furnace was designed by R. A. Wagstaff and B. G. Call, members of the staff.

16 McDougall furnaces, of six hearths, 18 ft. diameter.

14 McDougalls, six hearths, of 19½ ft. diameter.

The cars that take the roasted ore to the reverberatory furnaces are not covered. Hereafter, while being loaded they will come under a hood that has an opening, with a slight suction into a flue, for the collection of dust. This arrangement is not yet in use, but it has proved successful at the Tacoma smelter. Hoods have been built above eight new roasters and provision made to connect these hoods with the flue, but this improvement is being delayed by the need of covered calcine-cars. It is intended to cover the cars and to double their size; also to provide a tight connection between the hopper of the reverberatory and the car. All such betterments are delayed by the inability to obtain quick delivery of material. In these matters of dust-control the International smelter at Miami is so much better equipped that I venture to express surprise at the fact that the experience obtained there had not been utilized at Garfield. In my article describing the International smelter I gave details and also drawings of the appliances there in use.[2]

The feed to the roasters contains 14 to 16% copper, with 29 to 30% sulphur. After roasting it contains 16 to 18% copper, with 10 to 12% sulphur, having lost 12% moisture. The roasted ore is smelted in reverberatory furnaces, fired with pulverized coal, yielding a matte containing 42% copper and 25% sulphur. About 10% of the sulphur is eliminated in the reverberatory. The matte is treated in converters that yield blister copper 98% fine. This goes to the refinery at Baltimore, Maryland.

A question arose among our party as to the proportion of power used in the various stages of treatment to which the Utah

[2] See *M. & S. P.*, December 1, 1917.

Copper is subjected. It was ascertained that the refinery produced 170 lb. copper, the smelter 80 lb., and the concentrator 34 lb. per kw-day.

Returning to the question of moisture in the concentrate, it used to be the practice at Garfield to unload it upon belt-conveyors and bed it directly with the crude ore going to the blast-furnaces. At times as much as 10% of the blast-furnace charge was flotation concentrate, but the loss in dust was excessive. At the time of my visit shipments of flotation concentrate were being received from the Engels Copper Mining Co. in California. In order to minimize the cost of transport, this company reduces the moisture as much as is practicable, bringing it down to about 9%, which makes it slightly dusty. Apparently a 10% moisture is low enough for operations at the smelter.

On inquiry I was informed by Mr. Elmer E. Paxton, manager for the Engels company, that two Oliver filters are in use in his mill and that the de-watering of the concentrate is facilitated by a liberal use of steam, in three ways: (1) Steam is introduced through the emergency pipes, the air being excluded occasionally while the steam is admitted to the lifts. (2) Steam is forced through the feed-pipe to the bottom of the settling-tank, so as to warm, but not agitate, the concentrate just before a charge is drawn from the settling-tank into the filter-tank. While one charge is filtering, the next is being warmed. (3) A strong jet of steam is applied, through a pipe and hose at the back of the filter, so as to loosen and warm the bank of concentrate that forms in the bottom of the filter-tank. Thus the moisture in a two-inch cake is reduced as low as 10%. The average moisture in the concentrate shipped during May was 11%, this being reduced, by evaporation, to 9.5% by the time the concentrate reached Garfield.

The Ohio Copper company, at Bingham, has adopted the Lowden dryer. This machine is manufactured by the Colorado Iron Works, at Denver. It is designed to treat plastic material, such as flotation concentrate, without excessive loss in dust. The dryer consists (See Fig. 1 and 2) of a single hearth made of cast-iron plates *A*, beneath which is the flue *B*, through which

the gases of combustion pass. The feed is moved forward by means of rakes *C*, bearing rabbles *D*. These are right and left hand, in order to impart a ploughing action and distribute the material over the hearth. After the forward stroke, the rakes

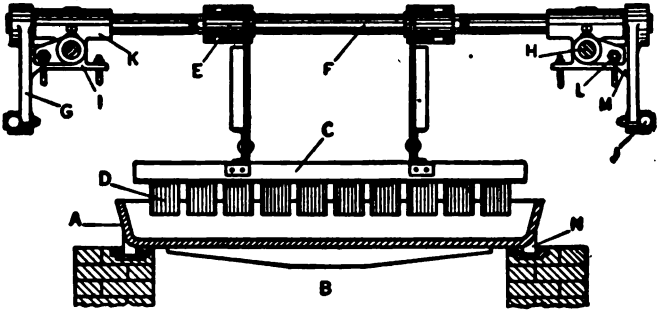


FIG. 1.

lift and clear the top of the material for the return stroke. The rakes move close to the hearth, preventing any caking, which would hinder the transmission of heat. The " balling " of the plastic concentrate is minimized by the fact that the length of the stroke is less than the distance between the transverse rows

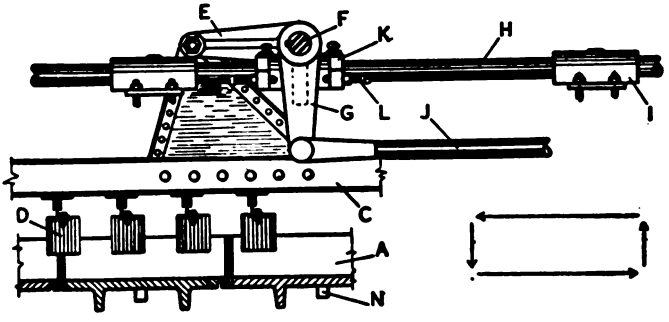


FIG. 2.

of rabbles, so that, in descending, they enter the material where it has been left in ridges by the preceding stroke. Any lumps are broken by a roller placed between two rows of rabbles at the point where such lumps are in the most friable condition. Ample provision is made for expansion and contraction wherever parts

are exposed to heat. The following data show the results obtained in practice at three plants:

Company.	Moisture in Feed, %	Moisture in Product, %	Coal Per Ton of Dry Solid, lb.
Federal Lead	15	5	117
St. Joseph Lead	16	5	125
Vindicator Consolidated	29	13	128

In each case the temperature of the feed was 55°, and that of the product 212° F., or the boiling-point of water. The concentrate from the Ohio Copper mill contains 12% moisture, with which the superintendent of the Garfield smelter is quite satisfied. On the other hand, Mr. Janney tells me that the moisture in his concentrate during April averaged 12.83%, in 425 cars containing 30,898 tons, each car carrying 72.7 tons wet or 63.36 tons dry. Apparently the stickiness of the Utah Copper product is due to the large proportion of insoluble matter in the concentrate produced by the pneumatic flotation-cells.

This problem of drying flotation concentrate, so as to deliver a product suitable for unloading, conveying, and sampling at smelters, must be faced. So far, whether at Miami, at Ray, or at Garfield, the mill-people have "passed the buck" to the smelter-people, who are tied by contracts that were signed before the true character of flotation concentrate was appreciated. I find that as between the managers of mills and smelters, the former always deliver a product containing less moisture than the same product contains on arrival at the smelter, despite such drainage and evaporation as may ensue in course of transit. This is a discrepancy that may be due more to a human factor than to one that is technical. It would be to the advantage of all concerned if the concentrate could be turned out in a form convenient to handle. Meanwhile the experiment being made with the dryer at the Ohio Copper is most interesting; there the dryer is placed at the discharge from the filter, as it should be, so that the concentrate drops from the filter upon a hearth of

A Battery of Stevens-Adamson Feeders.

the same width as the filter. I may add that a rake-conveyor was used to cool and convey hot material from the Argall roaster at the Portland mill near Colorado Springs, in 1902.

Would nodulizing be advantageous? That would be the next step after drying. Nodules of, say, half-inch size, would be most convenient to handle and would give a feed suitable for the reverberatory or even the blast-furnace. At Braden the flotation concentrate is adapted for the blast-furnace by nodulizing in rotating kilns,[3] heated by oil-burners to a temperature of 1750° F. The sandy concentrate, containing 17% silica, is heated to a sticky consistence, due partly to the combustion of the part of its sulphur content, so that the rolling motion causes it to ball into nodules. The kilns are sloped an inch per foot toward the discharge, from which the red-hot nodules drop upon an endless chain of cast-iron pans, which convey the product to hoppers that feed the blast-furnaces. In the course of this process the sulphur is reduced from 28% to 18%, and, of course, the moisture has been evaporated.

Nodulizing has been tried also by the Canada Copper Corporation at Princeton, British Columbia, by R. M. Draper.[4] A rotary kiln borrowed from a cement plant was used. The kiln was 7 ft. wide and 125 ft. long, or about 25 ft. longer than was required for the nodulizing of the copper concentrate. About 82% of the sulphur was retained in the nodules, this being important in a region where the sulphur is required for smelting. Pulverized coal from a neighboring mine was the fuel used, the kiln itself being operated by electric power. It was estimated that a 100-ft. kiln of this type would nodulize 100 to 125 tons of flotation concentrate in 24 hours. At Chrome, New Jersey, a similar experiment was made, by Mr. Draper, on flotation concentrate from the El Cobre mine, in Cuba. The consumption of oil, as fuel, was 6 to 7 gallons per ton of concentrate. The nodules proved satisfactory for blast-furnace smelting when charged cold, but there was trouble with crusts on the furnace

[3] *M. & S. P.*, February 12, 1916.

[4] "Nodulizing Flotation Concentrates." *The Canadian Mining Journal*, August 1, 1918.

when too many of the hot nodules were introduced, owing probably to the fact that " they were near the smelting-point when charged into the furnace and naturally smelted much higher up in the furnace." I quote Mr. Draper. The concentrate averaged 30% sulphur, whereas the nodules averaged 14%. One sample of nodules chilled immediately in water had a sulphur content of 20%. A screen-test of the nodules showed that all the product was under half-inch, but only 4.78% was finer than 16-mesh.

Desulphurization would accompany nodulization. A product containing 10 to 11% sulphur and about 16% copper would

Close View of Concentrate Feeder.

be most suitable for making a 40% matte. Unless desulphurized sufficiently the delivery of nodulized concentrate at the smelter would conduce to a low temperature in the roaster, so that the smelter-people would not regard this step as an advantage. In short, if any desulphurization is to be done at the mill, the operation must be completed to the point of rendering unnecessary any further roasting at the smelter itself. Moreover, the smelter company, in making a rate for treatment, includes a charge for expelling both the water and the sulphur in custom ores; it would lose this source of profit if the preliminary operations were performed at the mill. On a long haul, like that of

the Engels product, the removal of both moisture and sulphur would effect a considerable economy. Thus there are various conditions, technical and commercial, to be considered.

One would expect to find the Cottrell precipitator attached to the roaster, but at Garfield this precaution is only applied to the converters. How great the loss of copper in dust from the dryers would be, for example at Miami, if the Cottrell tubes were not used, was shown to me by L. O. Howard, the superintendent, who had the electric current turned off for a minute so that I might see the effect, which was to change a nearly colorless smoke into one heavily laden with dust. At Miami the flotation concentrate is not desulphurized, only dried, in the roasting-furnace.

At the Nevada Consolidated smelter, at McGill, Nevada, the gases from the roaster contain such an excess of water, owing to the high proportion of moisture in the concentrate, that it tends to condense with the sulphur tri-oxide, forming sulphuric acid, which attacks the brick of the flues and the iron of the jack-arches. At Garfield such trouble is avoided by causing the roaster gases to join the reverberatory gases, thereby maintaining a high temperature. The withdrawal of too much heat from the stack affects the dispersion of the fume and is likely to cause the destruction of vegetation. The wise smelter-manager avoids trouble in that direction.

Evidently the technical staffs of the mill and smelter should co-operate to solve this problem of drying the concentrate. As the proportion of table concentrate decreases, and more slimy flotation concentrate is produced, this phase of flotation practice will increase in importance.

PREFERENTIAL FLOTATION[1]

By W. Shellshear

By preferential flotation is meant the separation by flotation of one or more sulphides from each other. It is to be regretted that there is still much confusion of terms in describing flotation work. The American nomenclature which applies to selective flotation, indicating the separation of sulphide minerals from non-sulphide gangue, as distinct from preferential flotation or the separation of one or more sulphides from each other, however, well meets the case, and its adoption should be universal. These terms will need to be modified to some extent to cover the flotation of oxides and carbonates, but these are special cases. It is intended, rather, to deal here with facts gained from experience in operation and conclusions derived therefrom than to attempt to formulate a theory to account for the action of the different processes described.

Although the possibilities of preferential flotation were hinted at by Cattermole and others, it is only in recent years that processes have been devised that have made it a commercially profitable operation. The first of this type, which has proved successful in large-scale operations, was the Horwood process, in which certain sulphides have their surfaces rendered immune to flotation by roasting, leaving the surfaces of other sulphides unaffected. The success of this process largely depends, therefore, on careful attention to the detail of roasting such as the range of temperature, and the rate of feed. Large-scale operations, however, have demonstrated that, with modern mechanical furnaces, these factors can be kept well under control, and it is difficult to understand why this process is not in use for the

[1] From the *Mining and Scientific Press* of October 27, 1917.

treatment of many mixed sulphide ores, especially those containing lead, zinc, and iron.

It had long been recognized in the Broken Hill mills that when ore finely ground to a pulp was subjected to aeration, either by exposure to an air-surface, as in tabling operations, or else by a fall into a spitzkasten, cone, or similar apparatus, the galena and silver sulphide floated more or less imperfectly on this surface in preference to the zinc sulphide. This flotation was undoubtedly due to lubricating oil in the mill-circuit. Samples of the frothy scum from mill de-watering cones assayed in some cases as high as 60% lead, and 50 oz. silver per ton, but in all cases the scum was thin and represented only a small percentage of the sulphides present. Milling experience had thus demonstrated that there were some inherent properties possessed by the sulphide minerals, which were more marked in the cases of the lead and silver sulphides. Advantage was not taken of this fact, however, till Lyster proved that by controlling certain factors in the flotation treatment, use could be made of the relative differences between the natural properties of the various sulphides to effect their separation from each other. This was the first important step in the evolution of preferential processes. These distinctive properties of the individual sulphides vary somewhat with the different classes of ores. Thus, for example, they are found in a more marked degree in calcitic Broken Hill ores than in the rhodonite or garnet-sandstone variety. For this reason, even in apparently similar types of ore in the same locality, working conditions, as far as preferential flotation is concerned, need to be modified and adjusted to suit each particular case.

The controlling factors for preferential flotation of this type are the nature and amount of the agitation, variation in temperature, and proportioning of the medium used, the control of the air-supply during agitation, and the proportion of mineral salts in solution. It is believed by some that the preferential action in processes of this type is due to poor flotation. For instance, one writer, referring to Lyster's process, hints that it is probably due to imperfect conditions, the high grade of the lead being caused by only the finest particles of the lead floating, and that therefore

the residues probably are high. This is a mistaken idea, as there are large-scale plants, working on the Lyster principle, obtaining lead concentrate assaying as high as 60% in that metal while the residues averaged less than 2% lead. The secret of their success is the scientific adjustment of the controlling factors previously mentioned. Although these distinctive physical properties of the sulphides, by reason of which preferential flotation of this type was rendered possible, were present in a rather marked degree in slime freshly crushed from crude ore, it was found that if the slime were allowed to settle and accumulate in dumps these properties were seriously altered. This was probably due to oxidation and to concentration of salts in solution on the surfaces of the sulphides. Especially was this the case if the sulphide particles had dried from exposure, because it was then extremely difficult to obtain preferential flotation at all by such methods. As a rule if a dump-slime is treated on the Lyster principle a poor grade of "float" is obtained, consisting of mixed lead and zinc sulphides.

It was the continued research in the treatment of dump-products that resulted in a great forward leap in preferential work, the discovery of certain reagents or mediums, which, although used only in small quantities, could temporarily wet, or render incapable of flotation, certain sulphides, leaving the floatable properties of other sulphides unimpaired. It was found possible, by using these reagents in conjunction with various methods of flotation, to separate preferentially one or more sulphides from each other in an efficient manner, whether these products were freshly crushed or had been stacked in dumps. The fact that these reagents cause only temporary wetting, this effect being more complete when the reagent is still active as a medium in the solution, enables a sharp line of distinction to be drawn between these processes and those of the Horwood type, in which the faces of certain sulphides, such as those of zinc and iron, are permanently altered by the roasting action, rendering them for the most part permanently incapable of flotation.

Another type of process in which the Horwood effect is produced by chemical means is the ferric-chloride method. The

cost of chemical reagents generally makes a process of this type uneconomical.

The action of deadening reagents is extremely difficult to understand, as every medium at present known appears to act in a different way. Under certain conditions in a mixed lead-zinc sulphide-slime sulphuric acid will cause a preferential flotation of lead sulphide. This method was worked for some months as a commercial process treating the Central mine slime-dumps. Sulphuric acid in this case was added to the slime-pulp in the cold, no oil being used, although a certain amount of the soluble constituents from the oil used for the zinc flotation was returned with the circuit-liquor. In most cases the addition of fresh oil disturbed the preferential action. After floating the lead sulphide, using machines of the sub-aeration type, the zinc sulphide was floated by the addition of heat, more acid, and eucalyptus oil. This process is only workable in the case of certain Broken Hill slimes. In other cases, under practically similar conditions, a mixed-sulphide float is obtained. Even in a favorable slime the preferential action is upset by an excess of sulphuric acid.

In some cases, when experimenting with this method, one can obtain a float, the upper portion of which consists of lead sulphide and the lower portion of zinc sulphide, one sulphide gradually merging into the other. This process was discovered by Hebbard and Harvey, to whom also is due the successful development on a large scale of the under-driven suction-aeration machine for flotation.

The action of reducing gases, for example, sulphur di-oxide (Bradford's patent), especially if generated in the solution, is entirely different. Sulphur di-oxide when used in treating a mixed sulphide ore deadens each sulphide in succession according to their relative flotation properties. Thus, when treating an ore containing iron, lead, and zinc sulphides by this process, conditions may be so regulated that each sulphide may be floated in succession, the conditions being practically controlled by the amount of sulphur di-oxide gas in the pulp. An excess of sulphur di-oxide will, in most cases, render all the sulphides present temporarily immune to flotation, and in this case the surface

will merely be covered by a mass of thin white bubbles. Although a fine adjustment of conditions is required to float the sulphides in succession as described, in actual practice it is not difficult to float the lead and the iron sulphides as one product, leaving the zinc sulphide in the residue. It is interesting to note that once a sulphide is wetted it is practically impossible to re-float it as long as the sulphur di-oxide gas is in the solution. To float the wetted sulphide, heat and sulphuric acid usually are required. Although this process would appear to be delicate, the working conditions are not difficult to control in a well-designed plant, as proved by the fact that several large-scale plants are working successfully at Broken Hill using a modification of this method.

The action of sulphur di-oxide appears to be unaffected by the nature and amount of the salts in solution, within reasonable limits, and the amount of gas required is usually so small that its chemical action, if any, on the surfaces of the sulphides must be very slight. In some cases, to apply this process, the gas is passed directly into the solution, while in others it is generated therein by the addition of sulphuric acid and certain salts, such as sodium hypo-sulphite.

As another instance of the action of these agents I may take the case of potassium permanganate and potassium bichromate. Both are powerful oxidizing agents, and yet each acts in a different way. Potassium permanganate when added in small quantity to a lead-zinc sulphide slime will wet the zinc sulphide, and, provided conditions are correct, the lead sulphide may be floated as a high-grade product. The addition of sulphuric acid at normal temperature to the lead residue will cause a rapid and practically complete separation of the zinc sulphide from the gangue. This proves that the surfaces of the zinc sulphide are only temporarily affected. An excess of permanganate in the primary treatment will result in both sulphides being deadened and their subsequent flotation is usually difficult, even with heat and sulphuric acid. On a slime of a similar type potassium bichromate will cause a preferential flotation of the zinc sulphide, leaving the lead sulphide in the residue.

With this reagent the conditions required are usually more intense. Thus, in most cases a 0.2 to 0.5% solution of the reagent is required at a temperature of 120° to 140° F., whereas the potassium permanganate works at normal temperatures. In some cases a long digestion of the pulp with potassium bichromate is required to effect the deadening of the lead sulphide. Although this paper deals more particularly with the preferential flotation of lead-zinc sulphides, there are other sulphides which can be preferentially floated with these reagents. Potassium bichromate, for instance, will cause a preferential flotation of copper pyrite from iron pyrite.

In connection with the processes previously mentioned, the term "wetting" one sulphide in preference to another has been used. This term is employed by Bradford in describing his preferential processes, and as far as one can see, no other term adequately meets the case. When agitating a lead-zinc ore with one of these reagents in a glass vessel maintaining correct conditions, it will be found that one sulphide will be in a flocculent condition, and the other in separate grains similar to the constituents of the gangue. If the glass vessel with its contained pulp be now connected to a vacuum apparatus, and the air above the surface of the solution be evacuated, gas-bubbles will be plainly seen attached to the lead sulphide, but none to the zinc. It therefore seems reasonable to conclude that the function of these agents is to rob one or more of the sulphides of their gas, leaving the others with sufficient gas on their surfaces to admit of their subsequent flotation.

The sulphur di-oxide process points to a gradual displacement of gas from the various sulphides in rotation, according to their flotation properties, especially when it is considered that this gas is a powerful reducing agent. Possibly other agents of this class act in the same way.

To obtain a preferential flotation of zinc sulphide, leaving the lead sulphide in the residue, it is obvious that, as the flotation properties of galena are stronger than those of zinc-blende, the preferential agents must act in a different way. It will be found that in almost all cases of preferential lead flotation heat is not

required, and only comparatively small quantities of reagents are necessary. This is not the case with the preferential flotation of zinc sulphide, since in all known cases strong solutions and high temperatures are necessary, indicating that a chemical action takes place on the surface of the lead sulphide. Thus the bichromate action is probably due to the formation of lead chromate on the surface of the sulphide, and experiment has proved that in Bradford's salt-process a small percentage of lead is in solution as lead chloride. The fact, however, that the lead sulphide can be floated afterward in this process by the use of potassium permanganate and other salts indicates how comparatively slight must be the chemical action. It therefore seems probable that the flotation of any sulphide will be hindered in some degree by the presence in the solution of a salt which will chemically react with it. It was first pointed out in the case of Minerals Separation v. Elmore that, if virgin sulphides from certain localities were washed in ether and the ether afterward removed and evaporated, a residue was left consisting of a hydrocarbon oily in nature mixed with free sulphur which could be plainly seen in crystalline form. This has been verified by similar work on Broken Hill sulphides, but it has also been proved that some sulphide ores contain more natural oily residue than others. Whether there is any relation between the percentage of oily residue, the amount of adsorbed gases, and the flotative properties, remains to be proved. Experiments up to the present have indicated that dumps containing a relatively high percentage of this oily residue float more readily than those which do not. From the very small quantity of oil in a frothing-agent necessary to produce efficient flotation, it seems possible for the adsorption of gases on the sulphides to be accounted for if merely an infinitesimal trace of oily matter be present in this composition.

Although the principles underlying preferential processes are only imperfectly understood, by following routine conditions of working obtained by experiment in the laboratory and on the large-scale processes of this type, they may be made commercially profitable. A scientific control of such factors as rate of feed

and its regularity, quantities of reagents, and the like, is, however, vital.

Regularity of feed is essential. To call attention to the importance of this factor would seem unnecessary were it not for the fact that in many cases it is not given sufficient prominence. It is important in all metallurgical operations, but even more so in the case of preferential processes, because, without regularity of conditions, it is not practicable in many cases to work these methods at all. One must aim at getting feed and conditions of mechanical running as perfect as possible, the main axiom of all flotation-work being that without smooth running the accurate adjustment of metallurgical conditions is virtually impossible. In working a plant for the treatment of a mixed lead-zinc ore preferentially, irregular conditions will spoil both the lead and the zinc products, and neither will be of marketable value.

Control of aeration is also vital. Bradford was the first to discover that aeration could be controlled by a valve on the suction-pipe of a centrifugal pump, the air thus sucked in being atomized by the action of the impeller. Owen's patent shows a further development of this principle, the aeration in this case being controlled by a pipe connected to the bottom of an ordinary agitating vessel, the required air being sucked in and atomized by the agitator. It was found that by working on these lines the ordinary spitz-box used in the Hoover machine was unnecessary, the aeration and flotation being conducted continuously from the bottom and top of the same machine. In this type of flotation machine there are three distinct zones of action: (*a*) the aeration-zone, where air is sucked in by the impeller; (*b*) the atomizing-zone, where the air is completely broken up by the aid of baffles which also check the rotary motion of the liquid; and (*c*) the flotation-zone, a still zone on the top of the vessel where the flotation takes place. Similar control of aeration may be effected on either of these machines by replacing atmospheric air with air under pressure.

In considering the action of frothing-agents it must be said that it has now been definitely proved that, to float certain sulphides, oil, in the sense of an organic agent of any description, is

unnecessary. Thus, when preferentially floating galena by the sulphur di-oxide process no oil or organic agent as a general rule is required. There is at the present time a commercial plant giving a high recovery of lead with this process without the use of any medium of this description. In some cases oils or organic frothing-agents have been replaced by soluble inorganic frothing-agents, such as sodium carbonate. The function of the frothing-agents in most flotation processes is to intensify the physical conditions which promote flotation rather than to produce them. When experimenting with a mixed sulphide ore with a preferential agent, if a strong stream of atomized air be passed through the agitated pulp, the color of the sulphide which will float will be seen in the froth as it breaks at the surface of the solution before any oil or frothing-agent has been added at all. In the cases of most preferential processes the addition of certain unsuitable oils or frothing-agents will completely nullify the preferential action. For instance, the mixing of the pulp with an exceedingly small amount of oils of the wrong type before the addition of the preferential reagent will generally result in no separation of the sulphide minerals whatever. It is extremely difficult to separate two or more sulphides which have been floated with oil as a mixed concentrate in a previous operation, although this can be done with a process where intense conditions are used, as in Bradford's salt-process.

Although, as previously stated, the action of frothing-agents is to intensify the conditions of flotation, one of the many problems of preferential flotation is to use oils that will assist the flotation without disturbing the preferential action. As an example of a preferential process in which oil is not used, the sodium-carbonate process may be taken. Freeman discovered that by treating mixed lead-zinc sulphide slime with sodium-carbonate solution varying in strength from 1 to 10%, according to the ore treated, employing an iron vessel with ordinary conditions of agitation and aeration, the lead sulphide floated preferentially. The sodium carbonate in this process serves a double purpose, being a preferential reagent and at the same time a soluble frothing-agent. The addition of any oil is generally

deleterious to the successful working of the process, but in any case it is unnecessary, as the sodium carbonate usually gives a firm coherent froth. Although this process works quite successfully at normal temperatures, the grade of the lead concentrate is not affected by heating the solution up to 120° F. In a copper machine, on the other hand, sodium carbonate has a quite different action, for, if the temperature of the solution be raised to 160° F., a preferential flotation of zinc sulphide is obtained, leaving the lead sulphide in the residue. Even at normal temperatures the preferential flotation of the lead is imperfect if any copper is present as a part of the treatment-machine.

This is due to the fact that flotation conditions as a rule are materially altered if there is present in the solution even a trace of metallic salt such as a salt of copper, or mercury. If quantities of these reagents up to 2 or 3 lb. per ton be added to a pulp containing zinc sulphide or a sulphide of a similar nature, and the pulp be subjected to flotation-treatment, after flotation has taken place there is usually no trace of copper present in the solution. From this fact one is led to the conclusion that the action of these metallic salts is similar to the action of copper sulphate on scrap-iron, or, in other words, that the sulphides become coated with metallic copper or mercury, as the case may be. Bradford was the first to discover the properties of these metallic salts, and in 1913 he patented the use of reagents such as copper sulphate to exalt the flotation effect. Another interesting example of the action of copper salts is afforded by Bradford's salt-process. As is well known, this process consists in agitating a mixed lead-zinc ore with sulphuric acid in a salt solution varying from 7 to 10%, and heating the solution to about 140° F. The zinc sulphide floats preferentially, leaving the lead sulphide in the residue. After the zinc sulphide has been floated off, the lead sulphide may be floated by the addition of copper sulphate to the solution used for the flotation of the zinc, this being practically a continuous process. There seems to be large scope for this process, as it makes an extremely clean zinc concentrate, and yields a high recovery of zinc.

Different processes require different machines to obtain the

best results, and it is only by experiment on any particular ore that the best type of machine in any case can be determined. For instance, Bradford's salt-process will work successfully in the ordinary Hoover machine, whereas processes of the Lyster type usually work to advantage in the combination of pump and spitz-box machine illustrated in Lyster's patent. Permanganate of potash and agents of this type work to the best advantage in a sub-aeration machine, but they will give good results in the ordinary Minerals Separation apparatus. Every type of machine, however, usually requires different quantities of reagents and different conditions. Although I have not seen the Callow machine tried in this particular class of work, it seems to be suited for a number of these processes, and there is no reason why it should not work successfully. The action of metallic salts clearly demonstrates that the metal used in these machines, especially in laboratory machines, since commercial machines are usually made of iron or wood, is important, and for consistent results the laboratory machine must approximate the large-scale apparatus in its details.

As in ordinary flotation so in preferential treatment, in order to obtain good results two distinct phases are necessary. First, the pulp is brought into a physical condition for efficient flotation, and, second, aeration takes place, enabling the sulphide mineral that is to be floated to be separated as a froth. In the first place conditions are to be so adjusted that the mineral to be floated shall assume a clotted form, or, in other words, bound together in minute masses in the pulp. This clotted appearance is due to formation of primary gas-nuclei, and only under certain conditions will these nuclei form. If this primary phase is incomplete, aeration will cause a thin froth, which is troublesome to handle, and the recovery will be low.

In preferential flotation when deadening one sulphide, the other, if conditions are correct, will be in a clotted condition. If aeration be now applied an efficient flotation will take place. If, however, physical conditions are such that the action of the preferential reagent is imperfect, no amount of aeration will give good results, regardless of the manner in which it is applied.

The action of oil or frothing-agents appears to be mainly to increase the size and maintain the stability of the primary nuclei already referred to.

Every ore appears to have distinctive physical properties as far as its floatability is concerned and consequently the method of treatment of two different ores is rarely the same. This is particularly the case with lead-zinc sulphide ores. The varying composition of zinc-blendes from various localities to a large extent accounts for this. The properties of blende, as far as flotation is concerned, appear to be influenced by the amount of iron in its composition. Thus the zinc-iron blende, marmatite, having an approximate composition of 5ZnS.FeS, has quite different properties from a true "resin blende" of the composition ZnS, and even resin blendes differ to some extent in their properties. It is obvious, therefore, why one preferential process will work successfully on one class of sulphide ore and fail on an ore of a similar type. This has been previously illustrated in the case of the sulphuric-acid process, and other examples might be cited. Silver sulphide follows lead sulphide so closely in milling operations that for a time it was believed that the two sulphides were in chemical combination. Flotation has absolutely disproved this, since different preferential processes will in many cases give the same grade of lead concentrate from the same ore, but the concentrate will in some cases be high in silver and in others low. Indications show that silver sulphide is one of the most easily floated of all sulphides. The sulphur di-oxide process seems to be peculiarly adapted to the flotation of silver, and in many cases on obtaining a lead concentrate preferentially by this process the recovery of the silver is higher than that of the lead.

Preferential flotation is yet in its infancy, but most of the processes mentioned have worked or are in operation on a large scale and are not merely laboratory conceptions.

To test an ore for this class of flotation requires a great deal of experience and observation, as there are so many variable factors involved, and the disregard of minor details will usually affect the success of the treatment seriously. Preferential flotation has come to stay, and there are many fine-grained com-

plex ores which can be made commercially profitable by these methods. Mixtures of zinc and iron sulphides, fine-grained lead and zinc sulphides, and other ores of this type, are practically dependent on these processes for commercial separation. The scope for preferential flotation is, therefore, a large one, and these methods will soon be quite universally adopted.

FROTH-FLOTATION AT BROKEN HILL[1]

By C. C. Freeman

Introduction.[2]—Although great progress has been made in flotation of the Broken Hill silver-lead-zinc ores, no paper dealing with this subject has been presented to the members of the Institute since James Hebbard's valuable contribution in 1913.

Almost every discovery or development in the history of flotation has formed the basis of a patent, and but few experimentalists have overlooked the fact that their investigations might lead to the establishment of a patentable process. This, together with the aftermath of patent litigation, naturally resulted in secrecy being maintained in matters appertaining to the art, and the industry as a whole has consequently suffered considerably. Much valuable time has been wasted through numbers of men repeating work along certain lines, which, unknown to them, had already been thoroughly exhausted by others, whereas a lot of this would have been avoided by a freer interchange of information among those directly concerned.

Owing to differences in the ore treated and the various applications of flotation concentration in relation to gravity methods, the flotation problems of the various mines differ considerably. This, together with the secrecy previously referred to, has resulted in the development of numerous systems and machines, most of which would appear, to the casual observer, to comprise separate and distinct processes. I have endeavored to show how much these processes have in common with one another, and, at the same time, have tried to convey some general ideas on flota-

[1] From the *Mining and Scientific Press* of June 5, 1920.

[2] A paper read before the Broken Hill branch of the Australasian Institute of Mining and Metallurgy.

tion to those members of the Institute who are not directly associated with this branch of concentration.

Many theories have been expounded dealing with the underlying principles that control flotation, and while some of these appear to explain satisfactorily certain of the phenomena, a number of them are of little practical use, and are really only of academic interest. Generally speaking, the men who are directly connected with flotation operations are busily engaged attending to the practical and economic considerations, and have but little time to devote to the purely theoretical aspect, which perforce has to be left to the scientist.

Today all operators have certain general ideas on flotation, but few would dare to predict the result of treatment of an ore by any flotation method without first having recourse to a laboratory or other testing-machine. Undoubtedly, the experimental machine is still the mainstay of the flotation man for all research, investigation, and plant-control work.

Although several of the earlier flotation methods employed other principles, almost all the processes in use in Broken Hill today rely on the carrying power of air or gas-bubbles to which the floated material becomes attached, and this paper will only deal with this type of flotation, which is commonly called froth-flotation.

Developments in flotation have shown that most of the minerals possess surface properties which allow them to become attached to the air or gas-bubbles more or less readily. These properties are not, as was originally believed, confined to those minerals having the metallic-like surface of the sulphide minerals, but are also possessed, in some degree, by most other minerals and many artificially prepared salts.

The art of flotation depends on making use of the varying degrees of these properties possessed by different minerals, and, in cases where a separation is required of two minerals possessing the properties to approximately the same extent, by physically or chemically altering these surface properties of one of the minerals, so that one mineral will float more readily than the other.

It may be as well to point out, at this stage, that the terms

" preferential," " selective," and " differential " have been used to describe flotation methods whereby one sulphide mineral is separated from another. In Broken Hill these terms are practically synonymous, but for convenience, I have used " preferential " when referring to methods based on chemical alteration of the surfaces of one or more of the sulphide minerals, and " differential " for all other methods where no definite chemical alteration can be detected. It will be noted that the only difference is that in the former case a preliminary treatment alters the physical conditions of the surface of some of the minerals by bringing about a surficial chemical alteration of the mineral itself, and that the actual flotation separation then becomes identical with the " differential " systems. As will be shown, the general principles involved in the differential methods are the same as those in the older methods that separated the sulphide minerals from gangue minerals, producing what is known as a " collective " or " mixed " float. Certain conditions are necessary to bring about the attachment of sufficient air to an ore-particle to cause the latter to rise to the surface of the liquor. In the case of those minerals—such as some of the sulphides—which most readily become attached to the bubbles, flotation will result when the conditions are developed to only a slight extent, but these conditions must be intensified considerably to bring about the attachment of the air and a less readily floated mineral particle. By controlling the degree of intensification of conditions that brings about this attachment it is possible to separate a mineral which becomes readily attached to the bubbles from another mineral, the surfaces of which have a lower affinity for the same bubbles. Thus, if a mixture of evenly-sized particles of three minerals—(*a*), (*b*), and (*c*)—be subjected to flotation, and if, under the general conditions used, (*a*) possesses surface properties such that the air-bubbles become more readily attached to it than to (*b*), and (*b*) possesses such properties more than (*c*), it will be possible to arrive at a set of flotation conditions whereby (*a*) can be floated away from (*b*) and (*c*). By intensifying these conditions a point will be arrived at when (*b*) can be floated away from (*c*). If these latter conditions are used on the original mixture the float

would contain both (*a*) and (*b*). Thus, the general principles governing the differential flotation and the older collective methods are identical; but, while in the latter case the margin in surface properties in regard to bubble attachment between the least floatable sulphide minerals and the dull, oxidized, or gangue minerals is very marked, this difference is often small in the former case. In collective flotation, therefore, one may vary the flotation-intensifying conditions considerably without materially affecting the result, whereas preferential flotation is a much more delicate operation, requiring careful control in most cases. In view of the fact that the early work in flotation at Broken Hill was directed toward the recovery of blende from mill-tailing, de-leaded by gravity-concentration methods, and also that the blende required more intense flotation conditions than the other associated sulphide minerals, it was only natural that the conditions developed at that time were sufficiently intense to promote collective flotation.

Flotation ideas thus developed along lines that embraced the liberal use of several of the intensifiers, such as power, heat, acid, and frothing-agents. From this it became accepted, at that time, that flotation concentration could only be employed to separate minerals with a metallic-like surface (such as the sulphides) from materials with dull and easily-wetted surfaces. No doubt the fact that so much work was done on more or less weathered dump-tailing, in which the relatively low-galena content had become sufficiently superficially oxidized to reduce its flotation properties to at least as low as that of the blende, was responsible for the number of years which elapsed between the establishment of the collective and the preferential-flotation methods.

Differential Flotation.—As previously stated, the principles involved are identical with those used in the earlier collective-flotation methods, and differential results depend on the control and modification of those principles. The method depends primarily on the fact that, owing to the physical properties of the surfaces of minerals, the bubbles become more readily attached to the surface of some minerals than others, and, by regulating

the intensity of the conditions bringing about this attachment, it is possible to form bubbles carrying only the former minerals. The galena in freshly mined Broken Hill ore possesses the flotative property to a greater extent than the blende, and all the differential-flotation methods now used on this field recover the galena in the first float.

Much has been written in technical journals dealing with what may be termed the elements which produce the conditions necessary for the attachment of the mineral particles and the bubbles. A brief review of these may be of interest. The intensity of the flotation conditions produced is the sum of the effect of each of these elements, and those most commonly used are:

1. Air (or gas as CO_2 generated from carbonates in the pulp). This is essential in froth-flotation as a buoyant to carry the mineral. Within limits, the intensity will vary with the quantity of air introduced into the pulp.

2. Agitation. A certain amount of agitation appears to be essential to all flotation. It has been stated that the main function of agitation is to bring about an intimate admixture and distribution of the oil, and, while this is no doubt true to a certain extent, the fact that agitation is necessary when soluble frothing-agents are used would indicate that the function of agitation is not limited to the above. Agitation also plays an important part in cleansing the surfaces of the mineral particles, breaking up the air into minute bubbles, and promoting a coalescence between the oiled particles. The agitation need not necessarily be applied in the flotation machine, and, in some cases, the flow of the pulp through grinding machines, launders, and elevators, after the addition of some or all of the flotation reagents, will provide sufficient agitation for the removal of a readily-floated mineral. Owing to the large expenditure of power for agitation, this subject has received a lot of attention, which has resulted in the development of a great variety of flotation machines. The author's experience, however, has been that, with a given set of conditions, a definite expenditure of horse-power is required to produce a give nresult, and that frequently a saving in power can

be economically effected by increasing some of the other intensifiers or elements.

3. Frothing-agents, which consist of soluble salts, or, more frequently, oils. The American writers have classified oils as "frothers" and "collectors"—the former containing more or less constituents which are soluble in the flotation circuit, and the latter insoluble oils which coat the sulphide-mineral particles. A number of oils, particularly many of the Australian eucalyptus-oils, possess the properties of both frothers and collectors. In flotation practice in America great stress seems to be laid on the oil or mixture of oils used; but, while many different oils have been tried in Broken Hill, the eucalyptus and a few coal-tar products are the oils most generally used. American pine-oil or pine-tar oil is used to a limited extent in a few cases. The eucalyptus-oils used consist mainly of dextrapinene and phellandrene. Some of the oils characterized by being relatively low in phellandrene will, in many cases, give good results, but may require the addition of a certain amount of a "collecting" oil to make the float sufficiently stable. Usually a number of oils or oil-mixtures can be found that will produce identical results, and the final choice in the oil is decided by the cost factor.

4. Acid is a potent intensifier. It is universally used in Broken Hill in connection with blende flotation, excepting in cases where the ore is so calcitic that the consumption of acid becomes prohibitive.

5. Temperature invariably increases the intensity of the flotation conditions. Owing to the high price of fuel in Broken Hill, heating-plant circuits are somewhat expensive, and every endeavor is made to carry out operations at atmospheric temperature. Generally speaking, the end-point of a flotation separation is sharper and more clearly defined in hot than in cold circuits.

Within limits, similar results can usually be obtained by increasing one element and correspondingly decreasing another, so as to retain the same intensification of conditions. Thus, two plants working on similar material may obtain similar results, although in one case very little reagent and a lot of power are

used, whereas in the other less power but more intensifying reagents are employed.

Given two minerals with an appreciable difference in their flotative properties, a separation can be effected in a fresh-water circuit by applying some or all of the above elements, and, although this can be applied to the separation of galena from blende in many of the freshly-mined Broken Hill ores, the difference in the flotative properties of these minerals is often so small that such a process is rather too delicate and sensitive for ordinary purposes. Lyster discovered that the presence of salts, such as the sulphates of many of the metals in the circuit-water, retarded the flotation of the blende, and this principle has, either directly or indirectly, been applied in all the Broken Hill mills that are practising differential flotation. When using this system for differential galena-flotation, the blende is subsequently floated from the gangue by increasing the intensity of the flotation conditions by application of acid, heat, oil, or other intensifier. Some of the mines supply the necessary salts to their mill-circuits by using the underground mine-water, whereas those plants using H_2SO_4 in connection with their flotation operations create an ample supply of salts for differential-flotation purposes. The return circuit-water, besides containing these salts, also retains a certain amount of the soluble frothing constituents of the oils used. These conditions are favorable for differential galena-flotation, and advantage was taken of this by the Junction North Company (in its cascading plant), the Central Mine, and the Zinc Corporation (in its zinc concentrator). Very small additions of oil frequently improve galena-flotation without raising the blende under these conditions. Prior to the development of differential flotation it was recognized that if the percentage of these salts in the circuit-liquor became too high, blende flotation was difficult, even in hot, faintly-acid solutions. Thus, T. J. Hoover, in " Concentrating Ores by Flotation," referred to the fact that at the Zinc Corporation plant the blende flotation invariably went off when the quantity of salts in the solution exceeded 3000 grains per gallon.

Reference may be made to the fact that the ore from the

Broken Hill lode may be divided into two distinct classes, consisting of sulphide minerals (chiefly galena and blende) in a rhodonitic gangue on the one hand, and sulphide minerals associated with a gangue containing up to 10 or 12% of calcite on the other hand. The difference in the flotative properties of the galena and blende is slightly less pronounced in the rhodonitic than in the calcitic class of ore, so that differential flotation is somewhat more easily conducted when dealing with the latter ore; but in this case several of the methods which depend on the use of acids cannot be so economically applied, on account of the high acid-consumption involved.

The circuits necessary for the above type of differential flotation are so cheaply obtained that this method is used whenever possible. In some cases, however, the flotation properties of the galena and blende are so nearly alike that the presence of the salts in the circuit solutions will not sufficiently retard the blende to allow of satisfactory differential results. This occurs with some of the rhodonitic classes of ore, even when freshly mined, and in most of the tailing and slime that has been exposed to weathering. The Bradford SO_2 method is largely used for differential treatment in such cases. The presence of SO_2 in the solutions retards blende flotation to a greater extent than the salts referred to above, and this allows the use of conditions sufficiently intense to float even slightly tarnished galena particles without raising the blende. Subsequent flotation of the blende may be effected by removal of the liquor containing the SO_2, by removal of the SO_2 by aeration or heat, by decomposition of the SO_2 by chemical means, or by further intensification of the flotation conditions by acid and heat. A diversity of opinion exists as to whether it is essential to have salts in solution to obtain the best results with this process. As acid is used in all Broken Hill plants using the SO_2 process, this is of little account under normal plant-conditions, but is mentioned for the benefit of those engaged in laboratory work.

A new method was recently patented by T. H. Palmer, H. V. Seale, and R. D. Nevett, by which results similar to those yielded by the Bradford SO_2 process are obtained. The patentees claim

to make a solution of S by boiling tar or other oils in a weak solution of H_2SO_4 in the presence of an excess of powdered sulphur. Whether the sulphur goes into solution as an organic compound, or whether the sulphur removes the fractions of the oil that promote blende flotation, leaving a solution of only the fraction or fractions suitable for galena flotation, is not yet known. Whatever the action may be, the results obtained by the use of this process at the Junction North mine, where the process has displaced the SO_2 process, clearly demonstrate that the process yields the results claimed, and, in view of the fact that subsequent blende flotation can be obtained by heating the pulp to about 120° F., the process, where applicable, appears to be less costly to operate than the SO_2 process. When operating this process it is necessary to have soluble salts, such as the sulphates of some of the metals, in the circuit-water.

The methods outlined above cover most of the differential flotation at present in use in Broken Hill. Many other processes have from time to time been patented, but very few have actually been tried on a working scale. The permanganate method of T. M. Owen and H. V. Seale is claimed to give exceptionally good differential-galena results on weathered slime, but owing to the prohibitive price of this salt during recent years, the process has not been applied commercially. This process appears to embrace some of the anomalies so frequently encountered in flotation, in that, whereas the Bradford process applies SO_2 or other reducing agents, and Lyster uses a circuit containing soluble sulphates, etc., and bi-chromate has been claimed as producing differential-blende flotation, the permanganate (which is an oxidizer) yields a galena float, and the success of the process depends upon using a circuit containing a relatively small quantity of salts in solution. A soda-ash circuit will give sharp and clean differential-galena results on freshly-mined ore, when only little or no oil is used, and has the advantage that the subsequent flotation of even the coarser blende can be very readily obtained by the use of oil and a salt, such as $CuSO_4$. This process has been successfully applied elsewhere, and would be particularly useful in districts where sulphuric acid is difficult to procure.

The size of the mineral particles has an important bearing on results, and the larger the particles to be floated the more intense must the conditions be.. It therefore follows that, given conditions wherein galena particles have greater flotative properties than blende particles of a similar size—or, in other words when the intensity of the flotation conditions necessary to produce flotation of the galena are less than those necessary for the flotation of the blende—to float any larger particles of galena that may be present it may be necessary to increase the intensity of the conditions to the extent necessary to cause the finer blende particles to float. When dealing with relatively coarse particles of galena and blende, differential flotation becomes difficult, this being probably due to the high specific gravity of the galena compared with that of the blende, which causes the ratio of surface to weight to decrease more rapidly with the former than with the latter mineral as the size of the particles increases. A process such as the Bradford would, to a limited extent, allow a somewhat larger latitude in the relative sizes of the galena and blende particles submitted for differential flotation. Fortunately, very little coarse galena gets past the gravity-concentrating machines and reaches the flotation units; in fact, in all products from tables, classifiers, etc., there is a natural tendency for the galena particles to be smaller than the blende particles, and this materially assists differential galena-flotation.

Preferential Flotation.—It was early recognized that it was possible to alter the surface of some sulphide minerals so as to reduce their flotative properties and still leave the surface properties of other associated minerals unaltered. Most of the research work, aiming at the separation of galena and blende, was directed along these lines prior to the establishment of the Lyster process. A low-temperature roast was used in the Horwood process, and a lot of investigation was carried out to endeavor to obtain similar results by chemical means. The blende being a relatively stable mineral compared with the other sulphide minerals, it naturally followed that efforts were directed toward the alteration of the surface of the galena. Under this heading may be included the processes using oxidizers, such as ferric chloride, in hot acid solu-

tions, and the Bradford acid-salt method, the latter attacking and altering the surfaces of the galena, some of the lead from which passes into solution as a chloride. All these processes are characterized by the blende being floated before the galena, and nearly always result in a zinc concentrate containing relatively high silver-values. This is no doubt due partly to the fact that the silver minerals, being readily floated, tend to rise with the first float, and is also partly due to the silver from any soluble silver salts formed by oxidation, etc., being precipitated on the blende. In view of the fact that only small payments are made for silver in the zinc concentrate compared with almost full value for any silver in the lead concentrate, it is of prime importance to recover as much of the silver as possible in the latter product. This phase of the question affected the economic position to such an extent that investigations on these lines were almost abandoned soon after the establishment of the earlier differential-galena flotation methods. One may safely state that these preferential methods would be applied to lead-zinc-silver ores only in special circumstances, and then only when differential methods of flotation had failed. With the exception of the Horwood process, none of these methods is now employed at Broken Hill.

Machines Used.—The British Broken Hill Proprietary and the Zinc Corporation still retain the original M. S. type of machine, with separate mixing and spitz compartments, together with the underflow pipes. These machines give excellent service when a strong persistent float is produced, and have the advantage of the level of the pulp in each flotation compartment being under control. This control is of great importance when applying an acid treatment to ores containing varying quantities of calcitic materials, such as may be encountered when dealing with a mixture of material from several mines or tailing-dumps. In this case an increase or decrease in the quantity of CO_2 evolved reduces or increases the specific gravity of the pulp-gas-air mixture, and, unless the pulp-level in each cell can be independently maintained, it is difficult to control the froth-overflow. Apart from the gas factor, the single-level or staggered modification of this machine will, on fine material, give equally as good results

as will the original type of machine with the underflow pipes. Boxes of the above types, even when reasonably crowded, do not allow of a rapid removal of the froth when formed, and are not favored in cases where a tender froth is produced. The term " crowded " refers to a reduction of the area of the box toward the point at which the froth overflows, so as to increase the amount of froth reaching a given surface-area. This results in a quicker removal of the froth, and reduces the relatively dead surface-area away from the overflow-lip. The crowding should not be at too flat an angle, and the lip should be on a vertical side of a box rather than over a " crowded " side. The reason for this is that a larger amount of froth reaches the surface close to the crowded side, and this keeps the froth over the whole of the surface moving toward the lip, besides which the pulp at the surface close to a crowded side of a box is more agitated by ebullition than that at a vertical side, so that, if the lip is placed in the latter position, the chances of gangue being carried over mechanically are reduced.

The Central mill has adopted a single-level type of machine, in which the float is taken off the top of the mixing-compartment. In this case the necessary air is drawn in below the impeller, and the "still zone," necessary to allow the mineral-charged bubbles to rise to the surface, is produced by baffles arranged above the agitation zone. A modification of this type of box is to be seen at the British mine, North mine, and the Zinc Corporation differential slime-plants. In these instances the air is drawn through hollow over-driven vertical spindles operating more or less shrouded impellers near wearing-plates at the bottom of the boxes. The " horizontal " type of box has gained considerable favor of late, especially for slime-flotation, and is now used for slime treatment at the Junction North mine and Amalgamated Zinc works, and for all flotation purposes at the Block 10 mine. Several of the other mines are contemplating the installation of this type of machine in place of the existing ones. This machine gives good results, but the horse-power consumed per ton treated is on the high side. Centrifugal pumps delivering into crowded spitzkasten boxes are still favored at the Broken Hill Proprietary

mill, but, although this type of machine was for a time used to a certain extent in some of the other mills, they have since been replaced by machines of other types. One company uses a modification of the Owen machine for differential slime-flotation, but, owing to the exceptionally high power-consumption per ton treated it is questionable if this is the most economical type of machine.

Cascade Boxes or Pots.—This system, originally introduced by H. V. Seale and W. Shellshear at the Junction North plant, has been applied, for differential flotation, in a portion of the Central mill, and for blende flotation at the Amalgamated Zinc plant. Although, at first glance, this machine would appear to reduce considerably the power necessary for flotation, this is only true to a limited extent. When an ore, prior to reaching the flotation machines, has received almost sufficient agitation to produce flotation, the Cascade machine will yield a satisfactory float, but in other cases additional agitation must be provided before passing on to the Cascade unit. As in the case of the pneumatic machines, the Cascade pots will only give an incomplete recovery, unless the minerals are sufficiently prepared beforehand. Pneumatic machines have been tried experimentally by a few of the mining companies, but they failed to give satisfactory results.

Scope of Differential Flotation.—With the successful establishment of differential flotation, the opinion was expressed by some that Broken Hill milling practice would sooner or later be revolutionized by a general replacement of gravity-concentrating machines (such as jigs, tables, and vanners) by flotation methods. Flotation quickly displaced the vanners and tables operating on slime and fine mill-products, the recovery of the slimed galena from which had previously been a bugbear. It must be remembered that the galena that could not be recovered by tabling was in a fine state of division, and was, therefore, in an ideal state for differential flotation. Owing to the ease with which the coarser galena particles can be recovered by gravity concentration, and to the difficulty of differentially floating such particles, the local mills still retain their jigs and Wilfley tables for primary treatment. In the Central mill cascading has replaced all of the

primary tables, and the tailing from the former is lower than that previously yielded by the Card table. Rasmus J. Harvey has shown that the galena in the feed treated is all comparatively fine, and that that recovered from the Cascade plant is much finer than that previously recovered by the tables. This means that the galena in the tailing from this section is coarser when cascading is used than when the tables were used; but this galena, passing on to the zinc section, would be recovered more readily in their " de-leading " tables than galena in a finer state of division.

No doubt a certain amount of the work at present done by tables for the recovery of fine galena will ultimately be performed by flotation, and, in view of the fact that in a hydraulically classified product the galena particles are smaller than the blende particles, close classification should assist in bringing this about. On the other hand, jigs and tables are not expensive machines to run; they make good recoveries of the coarser galena in a concentrate that contains less blende than an equivalent flotation product, and the concentrates produced by the former methods are more easily drained and handled than those produced by the latter. In the light of present knowledge I am strongly of the opinion that the major portion of the gravity concentration now practised at Broken Hill will not be replaced by flotation.

The successful application of collective flotation for separation of the sulphide lead-zinc-silver minerals from gangue has been responsible for a revival of investigations of leaching methods for the recovery of lead and silver. Much research work with various solvents was carried out at the Broken Hill Proprietary prior to 1900, but, owing to high operating costs, such processes could not be economically applied to the relatively low-grade mill-products. Now that it is possible to obtain high-grade mixed sulphide products containing very little gangue, the possibilities of these methods have been greatly increased. The solution of the galena never did present any serious difficulties, and it is now claimed that high extractions of silver can be obtained in the presence of unaltered blende. These methods, yielding a much more complete separation of the lead and silver from the blende

than that obtained by any of the known differential or preferential flotation systems, will, with further development, be able probably to compete with flotation methods in many instances. The high operating costs of the solvent methods will, however, to a certain extent offset the increased lead and silver recoveries, and the scope for such systems can only be determined by economic results. Undoubtedly there is room for both systems in Broken Hill, and the solvent methods should be of special advantage for treating slime-mixed concentrate or slime-middling, which products are usually rich in silver.

Reference must be made to copper sulphate, the use of which has considerably increased during recent years. Although originally specified in a patent of Bradford's, it was not, so far as I am aware, used commercially in Broken Hill until 1916. Small quantities of copper or any of the highly electro-negative metals, such as gold, platinum, silver, and mercury, are rapidly precipitated from solution when added to a pulp containing galena and/or blende, and, while in the case of freshly broken galena no increase in the flotative properties is noticeable, an appreciable enhancement in the flotative properties of the blende ensues. This enhancement is usually sufficient to bring about the flotation of fine blende particles in neutral or alkaline circuits under conditions suitable for differential galena-flotation, but not sufficient to promote flotation of coarse blende without the addition of some strong intensifier, such as acid. It has been found, however, that the addition of about 0.1 pound of copper in a soluble form to an ore containing about 14% zinc will allow the blende to float with less acid than would otherwise be required. This is of special value when treating calcitic ore, and the practice at the zinc concentrator of the Zinc Corporation may be instanced, where tailing that would require 60–70 lb. of acid per ton under ordinary mineral-separation conditions needs only 25 lb. of acid to promote blende flotation after the addition of about half a pound of $CuSO_4$-$5H_2O$ per ton. All the copper added is precipitated and removed with the blende, so that the return-circuits are suitable for differential galena-flotation, if desired. Many of the parts of the earlier laboratory-flotation machines were con-

structed of copper or alloys containing copper, and small quantities of this metal passing into solution were no doubt frequently responsible for apparent anomalies between results obtained by different experimentalists. This factor probably retarded the discovery of many of the differential galena-flotation methods.

Flotation of Oxidized Ores.—So far, little has been done on a commercial scale in this respect, but at least two mills have in view the recovery of oxidized lead from dump material. As far as I know, the systems proposed include the superficial sulphiding (by H_2S, Na_2S, or similar reagent) of the oxidized galena, and the subsequent flotation of the same after the recovery of unoxidized galena and blende by ordinary methods. This method might be classed as a preferential method. It may be noted that the blende has higher flotative properties than the superficially re-sulphided lead minerals, so that the " lead " float is the last to be taken off. Unless there is sufficient unoxidized galena to allow a primary float of this to be made, it appears as if there would be a tendency for a lot of the silver to find its way into the blende product.

Conclusion.—I have endeavored to explain some of the phases of froth-flotation, especially as applied to local ores, from a practical point of view. Those who are closely associated with flotation work in Broken Hill will find that this paper contains nothing that is " new," but, as previously stated, any new discoveries in flotation have, to date, always been first described and published in patent specifications. Of recent years the practical side of flotation knowledge has made great strides, but many phenomena have not yet been satisfactorily explained. From time to time numerous theories have been advanced to try to explain certain flotation phenomena, but rarely, if ever, has a successful flotation process been evolved except by flotation experiments on a " hit or miss " principle.

A RESUME OF LITERATURE ON THE THEORY OF FLOTATION, WITH CRITICAL NOTES[1]

By H. R. Adam

In the following paper I propose to give a summarized version of the theoretical information that has accumulated within the last five or six years in connection with flotation processes for the concentration of ores. Papers on this subject have appeared chiefly in the scientific and technical journals devoted to mining and metallurgy, although it is noteworthy that physicists are now becoming more directly interested. Naturally the written information obtainable on both the practical and theoretical aspects of flotation is still very much scattered and as several important contributions to theory have been published without discussion or criticism it is by no means an easy matter to compare the data available or the statements founded thereon. The matter in this paper is classified not according to dates on which publications have appeared, but according to what have seemed to the writer to be the different phases of the subject, and in adding critical notes he is giving in a general way the results of his own observations and experimental work. For the sake of clearness it was thought advisable to include a good deal of what may be considered by many to be rather elementary and out of date information.

Conditions for Equilibrium when a Solid is in Contact with Two Fluids.—These are the apparent conditions in a mixture of ore particles and water during the application of the various methods of flotation; the ore particles represent the solid, while the fluids are water, more or less modified by the

[1] From the Journal of the Chemical, Metallurgical and Mining Society of South Africa. Reproduced in the *Mining and Scientific Press*, of November 27, 1920.

addition of various "reagents" and gas or gases, the latter in the form of minute bubbles. Before examining the statements of writers on flotation theory under this heading the equation representing the equilibrium as given by Clerk Maxwell[2] should be studied. "The equilibrium of the tensions concerned depends only on that of their components parallel to the surface because the surface-tension normal to the solid surfaces are balanced by the resistance of the solid. Hence for equilibrium,[3]

$$T_{sg} - T_{sl} - T_{lg} \cos \theta = 0,$$

whence

$$\cos \theta = \frac{T_{sg} - T_{sl}}{T_{lg}}.$$"

Poynting and Thomson[4] deduce a similar equation.

Edser[5] arrives at a similar result, although in a somewhat different manner. His reasoning is especially interesting, since he assumes that the tension T_{sl} is a residual tension. "When the liquid comes in contact with the solid the surface of the solid will be partly relieved of its strain by the attraction of the liquid molecules and similarly with the liquid molecules. Therefore when wetting takes place $T_{sl} = 0$, e.g., water/glass. When there is absolutely no wetting $T_{sl} = T_{sg} + T_{lg}$ and $\theta = 180°$, $\cos \theta$ in this case being -1; such a condition is approached by the contact of mercury and clean glass."

Edser, therefore, assumes that T_{sl} simply depends on T_{sg} and T_{lg}; this is doubtful, since new conditions may arise on account of chemical or electromagnetic action at the solid-liquid surface

[2] Clerk Maxwell, "Capillary Action," Encyclopedia Britannica, 11th edition, Vol. 5, pp. 261-263.

[3] In order to avoid confusion the symbols used by various writers, which naturally vary, have been put in the one form.

T_{sg} = surface-tension solid-gas.
T_{sl} = surface-tension solid-liquid.
T_{lg} = surface-tension liquid-gas.
θ = the contact-angle.

[4] Poynting and Thomson, "Properties of Matter," p. 140.

[5] E. Edser, "General Physics."

or interface.[6] According to Hatschek[7] there is no proof that in suspensions T_{sl} can be reduced to zero.

It will be seen from Clerk Maxwell's equation that an increase in the angle of contact means that T_{sl} increases relatively to T_{sg}. If we look at the matter from the aspect of the principle of minimum potential energy it becomes clearer. The greater T_{sl} the greater will be the tendency to reduction in the area of contact of solid and liquid, and it follows that θ will increase; conversely, if T_{sg} is large the tendency will be toward a reduction of the interface solid-gas, which can be done by the spreading of the liquid with consequent decrease of θ.

The following applications of this theory to flotation have been made:

O. C. Ralston[8] and Corliss and Perkins[9] state the relationships in the form used by Freundlich[10] for the distribution of colloidal particles in two liquid phases.

Since Ralston confines his statement to two liquid phases, oil and water, and since in modern flotation it is probably more correct to consider only the two fluid phases "contaminated water" and gas—only the statement according to Corliss and Perkins need be repeated.

(1) These writers state that either

(1) $T_{sl} > T_{sg} + T_{lg}$,

or (2) No one interfacial tension is greater than the sum of the other two.

They further state that the condition (3) $T_{lg} > T_{sg} + T_{sl}$ is impossible and that case (2) is the actual one in flotation. For complete wetting of gangue, for example, the condition is

[6] Langmuir, Jour. Am. Chem. Soc., 1916, and *Met. & Chem. Eng.*, Oct. 15, 1916; also McLewis, "The Chem. Theory and Capillarity," *Science Progress*, April, 1918. Harkins, Proc. Nat. Acad. of Sciences, December, 1919.

[7] E. Hatschek in discussion on Sulman's "Contribution to the Theory of Flotation," Bulletin, I. M. M., January, 1920.

[8] O. C. Ralston, *M. & S. P.*, October 23, 1915.

[9] H. P. Corliss and C. L. Perkins, Jour. Ind. & Eng. Chem., May, 1919

[10] Freundlich, *Kapillarchemie.*

$T_{sg} > T_{sl} + T_{lg}$; while conditions (1) and (3) would imply complete non-wetting.

This argument is in accordance with the Clerk Maxwell equation, but it must be pointed out that condition (2) implies that a triangle could theoretically be constructed with sides proportional to the three tensions. According to Clerk Maxwell, both experimental work and theoretical reasoning support the view that this condition is imaginary and where it apparently occurs, one or more of the surfaces is contaminated; that is, where spreading of the liquid does not occur we are not dealing with true contact of the surfaces. It is, however, probably quite justifiable to consider the case in the manner of Corliss and Perkins, since in flotation the surfaces almost certainly are contaminated, but due consideration of the matter is important in view of the discrepancies in the results obtained for contact-angles, to be mentioned later.

Taggart and Beach [11] state the equilibrium equation as

$$T_{sl} = T_{sg} + T_{lg} \cos\theta, \text{ from which}$$

$$\text{Cos } \theta = \frac{T_{sl} - T_{sg}}{T_{lg}}.$$

This means that a large contact-angle will be the result of a low T_{sl} and relatively high T_{sg}, that is, a tendency for the liquid to wet the solid, which is obviously incorrect. Sulman [12] gives the relationship in the manner of Edser,[5] and evidently regards the tension at the solid-liquid interface as a residual tension greater or less according as wetting is partial or complete. Sulman's explanation of the matter is made the more lucid since he discusses the various possibilities according to the variation of the contact-angle between 180° and zero.

In a paper on the theory of wetting, Cooper and Nutall [13] state the equilibrium equation and give a clear explanation of the conditions that may obtain. As these writers have ap-

[11] A. F. Taggart and F. E. Beach, Bulletin, A. I. M. E., September, 1916.
[12] H. L. Sulman, Bulletins, I. M. M., Nov. and Dec., 1919, and Jan., 1920.
[13] W. F. Cooper and W. H. Nutall, *Jour. Agri. Sci.*, Vol. VIII, 1915-16.

proached the matter from an entirely different standpoint from that of flotation, it is of interest to summarize their article even at the risk of considerable repetition. They quote Quincke as being the first to state the conditions for wetting which, using the same symbols, are:

(*a*) That T_{lg} should be low.
(*b*) That T_{sg} should be high.
(*c*) That T_{sl} should be low.

Cooper and Nutall emphasize that in regard to wetting it is not sufficient to regard only the surface-tension of the liquid, since even though T_{lg} be high, wetting may occur if T_{sl} is low. The factors influencing T_{sl} are:

(1) The chemical or solvent action of the liquid on the surface layer of the solid; (2) adsorption of dissolved substances at the liquid surface, which occurs when such a concentration causes a decrease in the surface-tension of the liquid. The point made with regard to this adsorption is that it is accompanied by increased viscosity at the surface, and that there appears to be a close connection between superficial viscosity of liquids and their wetting power for solids; further reference to this will be made in a later paragraph. From the point of view of flotation the value of the work of Cooper and Nutall lies chiefly in the emphasis laid on the interfacial tension T_{sl}. In the cases which they are considering, namely, the wetting power of dips and insecticides, the possibility of chemical or solvent action at the solid-liquid interface is obvious. In flotation the complexity increases, and we have to consider possible factors influencing T_{sg} and T_{lg}, while the work of Langmuir and Harkins already referred to indicates that new conditions may arise at the solid-liquid interface affecting T_{sl}.[7]

The Contact-Angle.—From the foregoing discussion of the equilibrium equation it is clear that the contact-angle is practically the only quantitative guide to the relative tensions. It may be remarked at once that from the practical point of view, measurements of contact-angles are probably of little value in

flotation. Even with the utmost precaution against contamination physicists are unable to arrive at close agreement, and it is evident that the most minute alterations in the conditions obtaining at the surfaces of the three phases may affect the angle considerably.

Freundlich [10] expresses considerable doubt on the question of contact-angles and states that where a positive angle is obtained it may be due only to contamination of the surfaces. He further states that it is generally concluded that complete wetting means a zero contact-angle. In the case of metals, however, the evidence is in favor of a positive angle though the results are in such poor agreement that they can hardly be relied on quantitatively. In the case of glass and water it appears almost certain that if a clean surface is dealt with the angle is zero; for metals Kaye and Laby [14] give the angle as varying between 3° and 11°.

To the writer's knowledge the only two papers on flotation theory giving data on contact-angles are those of Corliss and Perkins [9] and Sulman.[12] The former contributors do not attempt direct measurement of the angles but give the related values of the rise of the meniscus of the liquid against the mineral surface.

For pure water, taking the rise against the surface of the silicate (which silicate is not mentioned) as unity, the rise against chalcocite is 0.5, and for chalcopyrite 0.8; for 0.1% H_2SO_4 the ratios are, silicate 1, chalcocite 0.6, chalcopyrite 0.8, and for 0.1% NaOH, silicate 1, chalcocite 0.9, and chalcopyrite 0.9. Corliss and Perkins also found that when the second fluid was an oil-mixture such as is used in flotation, instead of air, the contact-angle of the mineral with the water was over 90°.

The most recent figures for the contact-angles of minerals and water are given by Sulman.[12] It is stated that minerals have a maximum and minimum angle with water and the difference between the maximum and minimum is called the "hysteresis." Sulman states that the hysteresis has important effects in flotation. The most noteworthy points in Sulman's investigation are (1) The magnitude of the angles, for example:

[14] Kaye and Laby, "Physical and Chemical Constants."

	Minimum	Maximum
Stibnite	24.0°	62.8°
Calcite	39.6°	85.5°
Glass	33.0°	39.5°
Quartz	19.5°	58.5°
Chalcopyrite	37.0°	87.0°
Galena	35.0°	73.0°

(2) The small differences between two such minerals as quartz and stibnite (stibnite is one of the most easily floated sulphides).

(3) The hysteresis—Corliss and Perkins [9] also refer to this hysteresis and suggest an explanation on the basis of the smoothness of the mineral surface. Sulman refers to a "molecular interlocking of the liquid and the solid."

In view of the doubt regarding contact-angles, Sulman's figures are distinctly surprising and can hardly be accepted as final, although it is stated that the figures have been confirmed by two different methods. The writer has made several attempts to arrive at satisfactory conclusions for the contact-angles of a few minerals with water. The results obtained were somewhat varied, but, on the whole, indicated that when examination is made immediately after immersion in water the contact-angle is either zero or very small in the cases of chalcopyrite, galena, marcasite, stibnite, quartz, and calcite. The faces examined were, however, not natural cleavage-planes but surfaces obtained by polishing with a fine jeweller's file. There is, however, a distinct difference in the behavior of these minerals. The sulphides only give the zero angle if examined directly after being immersed in water; if the surfaces are merely touched with a piece of filter-paper and then examined again, positive contact-angles up to 90° or more are easily obtained. The inference is that sulphides "adsorb" films of air or oxygen with extreme rapidity and in this condition resist the spreading of the water to a greater or lesser extent. It is hoped to give the method of procedure and more detailed results of these investigations at a later date, at present the results are hardly conclusive.

Adsorption of Gases at the Surfaces of Minerals.—Although several writers on flotation—Rickard, [15] Sulman [12]—

[15] T. A. Rickard, *M. & S. P.*, July 14, 1917.

have stated that the adsorption of gases on mineral and metallic surfaces is of minor importance in flotation, the evidence in experimental investigations is to the contrary, at least as far as theoretical explanations are concerned. The probabilities are that the tendency which nearly all solids show to condense or adsorb gas on their surfaces is closely connected with the variability of the contact-angle and consequently with the interfacial tensions of solids with liquids and gases. It is true that oil is used in nearly all recent flotation methods, but there is no reason to suppose that this involves great changes in principle since the essential features can easily be manifested without oil. The fact that oil or oils are necessary in practice has tended to obscure the main problem, which is the cause of the preferential adhesion of gas-bubbles to sulphides and metals. Unfortunately the knowledge of the causes and effects of gas adsorption on solid surfaces is very limited. Sulman states that "Edser has disproved the air-film theory since such a condensation must involve a considerable quantity of gas . . . readily appreciable by chemical and physical means." He further states that

"(1) Pure air is not condensed to any appreciable extent on blende, quartz, or galena.

"(2) That CO_2 is minutely adsorbed.

"(3) That a gas-free mineral floats at an air-free water surface, that is, *in vacuo*, with the same ease as at a water/air surface."

These statements are of a controversial nature. It is well known that solid surfaces, particularly metals, do adsorb or condense appreciable quantities of gases and although this property is not commonly referred to in the specific case of minerals, it is not likely that the latter are peculiar in this respect. In any case there is abundant evidence of a less exact nature that sulphides especially, do adsorb gases readily and that the gaseous films are extremely difficult to remove.

Whetham [16] remarks on "the film of condensed gas which seems to exist on all solid surfaces and to be so difficult to remove." He further refers to the work of Brown, Spiers, and Erskine-

[16] Whetham, "Theory of Solution," pp. 269-272.

than the nature of the solid. This is not altogether in agreement with such evidence as is available in flotation investigations, but it may be remarked that Freundlich's statement is apparently based on experimental results on such porous solids as charcoal, meerschaum, etc. The fact that carbon di-oxide is more difficult to remove than air is, however, in accordance with Freundlich's statement that the more easily liquefied gases are more strongly adsorbed.

Froths and the Effect of Oil.—This phase of the subject has been dealt with very fully by several writers on flotation theory including Rickard,[17] Hildebrand,[19] Taggart and Beach,[11] and notably Sulman.[12] The conditions for a stable froth are clearly set out in works on colloidal chemistry. Lord Rayleigh[20] has shown that frothing is always associated with contamination; in fact, in comparison with other features of flotation the stabilizing of the froths is thoroughly well understood. It is of special interest to note, as has been done by Sulman and others, that the mineral particles themselves may provide the stabilizing conditions; this is what is meant by the term "armoring" of the bubbles. Thus it may be shown in many cases that when only a small proportion of sulphides is present in an ore these may float but be unable to form a coherent froth since there is insufficient armoring. With an ore-sample containing exactly the same constituents, but a larger proportion of sulphides, a comparatively stable froth may be obtained. Sulman states that the surface-tension of water is considerably lowered by the presence of mineral particles. If this is correct it may partly explain the fact mentioned by Mickle,[17] Henderson,[18] and Hoover,[21] also confirmed by the writer on stibnite ores,[22] that the presence of much slime in flotation without oil gives uniformly unsatisfactory results.

It is well known that it is easy to overdo the addition of what are called "frothers" in flotation and to obtain a "barren"

[19] Hildebrand, *M. & S. P.*, July 29, 1916.
[20] Lord Rayleigh, "Lecture on Foam," Proc. Royal Inst., March, 1890.
[21] Hoover, "Concentrating Ores by Flotation."
[22] H. R. Adam, Jour. C. M. and M. S. of S. A., June, 1915.

froth (Sulman, Rickard, Corliss, and Perkins). The reason generally given is that the surface-tension liquid-gas has thereby been so greatly lowered that the wetting tendency is increased. In the discussion on the equilibrium equation, however, it was shown that wetting power depends on other factors than the surface-tension of the liquid, notably the viscosity.

In most of the papers on flotation theory already referred to, the effects of the oil additions are fully discussed. The main effect, although there is no definite evidence on the point, is that the oil spreading rapidly over the sulphide surfaces forms films of extreme tenuity, with the result that the characteristic properties of the sulphide surfaces, as far as the adhesion of gas-bubbles is concerned, are so greatly enhanced that practical flotation depends chiefly on these small additions of suitable oils. Sulman gives figures showing greatly increased contact-angles for oil-filmed minerals in 0.7% sulphuric acid.

Additional Bibliography.—Owing to the method on which this summary of flotation literature has been prepared the references on the subject cannot claim to be complete.

For much useful information, both on the theory and practice of flotation, the columns of the *Mining and Scientific Press* for the last five or six years should be consulted. Most of the articles which have appeared in that journal are collected in a convenient volume edited by T A. Rickard.[23] The books on flotation by Hoover [21] and Megraw [24] also contain chapters on the theory of the subject. The effort required to follow the voluminous reports of legal proceedings over flotation patents is not likely to yield sufficient reward to make it advisable. For a non-mathematical treatment of surface-tension the reader is referred to "Surface Tension and Surface Energy" by R. S. Willows and E. Hatschek. The most noteworthy contribution to flotation theory which has recently appeared is that by H. L. Sulman, which has been several times referred to. His paper contains a vast amount of valuable information and several portions of it are criticized in the discussion which followed.

[23] T. A. Rickard, "The Flotation Process."
[24] Megraw, "The Flotation Process."

Truscott [25] questions the application of the term "adsorption" to the adhesion of sulphide particles to gas-bubbles and the use of the term "suspensoids" for a mixture of ore particles and water. He questions if there is any fundamental difference between film and froth flotation.

Porter [26] criticizes Sulman's idea that a zero contact-angle is not accompanied by complete wetting and questions the extremely high value for the contact-angle water/glass.

Hatschek [7] criticizes Sulman's statement that complete wetting means a reduction of interfacial tension to zero and points out that far-reaching conclusions are based on very meagre experimental evidence.

It is impossible to summarize satisfactorily this important paper, but there are portions not already referred to which should be mentioned. Sulman insists on the importance of "flocculation" in flotation and states that in order to be floated the mineral must first be "flocculated." Flocculation has been considerably studied in connection with the settlement of slime—Free [27]—but in articles on flotation I have found the term used only in the paper by Corliss and Perkins. The latter, although not very lucid on the matter, apparently conclude that flocculation is harmful in flotation since the aggregates formed may consist of silicious gangue particles which may float with the sulphides. If Sulman's statements are interpreted correctly, however, the trend in flotation practice is to float preferentially almost any desired mineral by causing it to flocculate; this is to be done by various modifying physical and chemical factors. These ideas are in all probability the result of the wide application of flotation to the treatment of "slime," which is commonly classed as a colloidal solution. The natural inference to be drawn from Sulman's paper is that there are considerable differences in principle between the methods of flotation he chiefly refers to, and what may be called the film-flotation of comparatively large particles which, as has already been mentioned, is

[25] J. A. Truscott, Bulletin, I. M. M., Dec., 1919.
[26] A. W. Porter, Bulletin, I. M. M., Jan., 1920.
[27] E. E. Free, *E. & M. J.*, Feb. 5, 1916.

best accomplished in the absence of slime. Possibly this theory of flocculation accounts for the fact that the concentrate obtained by the Minerals Separation methods seem generally to contain a high proportion of gangue.[28] A further important feature of this paper is the reported effect of acidifying the liquid. It is stated that the contact-angles are generally lower in acid solutions; from this it would probably follow that the surface-tension of water is decreased by the addition of acids. Taggart and Beach confirm this to some extent, but according to Taylor,[29] also Kaye and Laby,[14] the effect of the acid is to slightly increase the surface-tension of water. The most obvious effects of adding acid, in the writer's experience, are that the sulphide surfaces may be freed from oxide films (this is particularly noticeable in the case of banket ore containing pyrite), and that an additional supply of gas-bubbles may be provided in cases where carbonates are present.

Concluding Remarks.—As a result of the commercial success of flotation, many new facts have been learned empirically regarding the physical and chemical properties of surfaces. Exact experimental data are, however, required before sound generalities can be established. It seems to the writer that a statement such as the following is, at present, as much as is justifiable. A tendency for such surfaces as those of metals and mineral sulphides to adsorb and retain films of gas or grease to a greater degree than the surfaces of substances such as quartz and silicates is generally indicated. · Such adsorption, according to the theory of adsorption in liquids, must be a manifestation of greater surface energy in the case of the former substances. Having obtained such films, the solids must be regarded as contaminated, and we no longer have true contact between the solid and the two fluids; the energy of the solid surface being reduced to a minimum by such adsorption, the surface energy liquid/gas is manifested by a decreased adhesion of the liquid to the solid, with the result that the gas-bubbles cling more or less tenaciously to the solid surface. The aggregations or "floccules" of

[28] Report on legal proceedings over flotation, *M. & S. P.*, Sept. 29, 1917.
[29] W. W. Taylor, "The Chemistry of Colloids," p. 237.

gas and solid particles thus formed may in certain circumstances sink, but in most cases will rise, owing to the great volume of adhering gas.

If it is true that such metallic surfaces have this greater surface energy, such a fact suggests a connection with the fact that metals and sulphides more readily undergo chemical transformation than quartz, silicates, and oxides generally.

It is somewhat disheartening to the metallurgist on taking up the study of flotation theory to find that the obtaining of experimental data is really a matter for the physical laboratory and that the interpretation of results is by no means easy. Hatschek, in discussing Sulman's work, speaks rather sarcastically of the mass of empirical information imparted and the explanations given of the facts. The assembling and reporting of observations of a purely empirical nature must, however, be of great importance in the construction of a general theory. In actual fact the litigation that has taken place over flotation has, among other things, demonstrated that even among physicists, there is almost complete ignorance as to the real meaning of the phenomena that attend the wetting of a solid by a liquid. Hatschek himself admits this,[7] and suggests it may be due to "a lack of any important problems involving a closer knowledge of these factors." The fact is, however, that the importance of a theoretical study of the phenomena concerned, is not by any means confined to flotation. The references to Whetham's "Theory of Solution," and to the article by Cooper and Nutall on "The Theory of Wetting" in connection with dips and insecticides should make this clear.

There are similar problems involved, in the soldering and welding of metals, in the amalgamation and cyaniding of gold, and, of even more direct interest on the Rand, they have an intimate bearing on the difficult questions concerned in the settlement of fine floating dust particles underground.[30]

[30] J. Moir, "Recent Investigations on Dust in Mine Air," Jour. C. M. and M. S. of S. A., July, 1915.

INDEX

Acid, addition of, 10, 211, 683
  as affecting flocculation, 371
  as reducing agent, 387
Adam, H. R., 670
Adhesion, 269, 307
Adsorption, 375
  of gas, 677
  selective, 59
Aeration, control of, 648
Afterthought mill, 593
  flow-sheet of, 597
Agitation, 164, 658
  by air, 20
  machine, 174
  mechanical, 188
  submerged, 187
  tests, 170, 223
  time of, 201
Agitators, 424, 561, 568
Air, action of, 7, 13, 22
  adhesion to mineral, 68
  agitation by, 20
  cell, 180, 471
  jets, 549
  pans, 406
  through porous medium, 126
Alkaline chlorides, 383
  permanganate, 391
  solutions, 389
  sulphides, 390
Alkalinity, 184
Allen, Glenn L., 486
Analytical work, 165
Anderson, Robert J., 277
Angle of contact, 49, 323, 673
Argo mill, flotation in, 93
  flow-sheet of, 94
Arizona, flotation in, 530
Arsenides, 517
Arthur mill, 616
Atckison, E. J., 536
Atwater, M. W., 418
Australian practice, 245, 273, 569, 654

Bacon, Raymond F., 379, 489
Bains, Thomas M., Jr., 254, 258
Ball-mill, discharge, 597
  Krupp, 208
  use of, 83
Ballot, John, 19, 110
Bancroft, Wilder D., 61, 75, 330
Beauchamp, F. A., 12
Bibliography, 377, 681
Blende ore, treatment of, 553
Block, James A., 254
Blower, Crowell, 176
Boom-stackers, 244
Bornite, flotation of, 25
Bottle-tests, 169
Bradford, Hezekiah, 4
Bradford, Leslie, 385, 551
Bradford process, 559
Brine, leaching with, 519
Broken Hill Proprietary, 250
  flotation at, 9, 21, 29, 196, 249, 273, 527, 545, 569, 654
Brown, J. I., 445
Bubble-films, 274
Bubbles, 51, 525
  color of, 53
  function of, 342
  levitation of, 2
  physics of, 37
  the armor of, 325
Buechner filter, 177
Butte, flotation at, 25

Butte & Superior Mining Co., 23, 120
Butters, Charles, 214

Calcium sulphide, 502
California, flotation in, 402, 425, 429
Callow, J. M., 28, 254, 261, 262, 466, 503
Callow cell, 62, 125, 135, 409, 536
  machine, 153, 156
  tester, 161
Canby, R. C., 27
Capillarity, 39, 305
Capillary tubes, 319
Capital outlay, 523
Cascade method, 524, 579, 666
Case machine, 147
Cattermole, Arthur R., 14, 103
  process, 199
Central mill, 665
  flotation at, 17, 580
  flow-sheet of, 571, 583
Centrifugal pumps, 209
Chalcocite, flotation of, 25, 71
Chapman, G. A., 17, 26, 200
Chile, flotation in, 429
Chino, flotation at, 505
Chloride of lime, 393
Chlorides, alkaline, 383
Chlorination of concentrate, 232
Chromates, 382
Circuits in mill, 661
Clennell, J. E., 215
Coal-tar flotation-agent, 50
Cobalt, flotation at, 509
Coghill, Will H., 261, 274, 300, 325
Cohesion, 278
Cole, David, 475
Collective flotation, 598, 667
Colloids, 283, 344, 354
  affected by free alkali, 373
  bibliography of, 377
  classification of, 361
Colorado, flotation in, 423
Concentrate, chlorination of, 232
  concentrating of, 438
  cyanidation of, 214
  de-watering of, 415, 439
  drying of, 600, 635
  grade of, 138
Concentrate, heating of, 411
  marketing of, 517
  nodulizing of, 638
  roasting of, 220, 432, 601, 633
  silica in, 430
  smelting of, 431, 626
  treatment of, 82, 214
  unloading of, 433, 631
  vanner, 615
  zinc, 212
Condensation of gas, 280
Contact-angles, 49, 323, 673
  differences, 351
  films, 285
Contaminant, 40, 57
  oil as a, 279
Copper ores, oxidized, 503
  recovery of, by leaching, 586
Corliss, H. P., 334
Cost of Horwood process, 608
  of plant, 85, 194
  of re-grinding, 89
Costs at Dutch-App, 92
  comparative, 591
  in California, 89
  in Mexico, 191
  operating, 412, 520
Courtney, C. L., 199
Coutts, J., 160
Cripple Creek, flotation at, 79
Critical temperature, 303
Crowder, Samuel, 6
Crowell blower, 176
Cyanidation of concentrate, 214
  of tailing, 234
  v. flotation, 86, 95, 193, 541

Deadening reagents, 644
De Bavay, A. J. F., 10, 252
Delprat, G. D., 9, 250, 545
Delprat process, 251
Devereux, W. G., 86
De-watering of concentrate, 415, 439
Differential flotation, 378, 396, 657
  methods, 679
Dilution, 185
Discovery of frothing process, 205
Disposal of products, 415

Disposal of residue, 237
of slime, 247
Dissolved substances, 293
Distributing tailing, 241
Dorr thickener, 237, 560, 565
Drainage-belts, 242
Drops, spreading of, 295
Dryer, Lowden, 635
Drying of concentrate, 600, 635
Dump-slime, treatment of, 572
Durell, C. Terry, 248, 282
Dutch-App, costs at, 92
flotation at, 91
Dye, Robert E., 520

Eberenz & Brown, 445
Electrification of particles, 254, 265
Electro-static phenomena, 285
Elmore, Francis E., 5, 21, 114
Elmore machine, 152
oil process, 13, 22
vacuum process, 250
Emulsification, 77
Emulsions, 283
stability of, 296
Emulsoids, 363
Equipment, pneumatic, 168
Everson, Carrie J., 3, 9
Experimental plant, 203
Experiments, 41, 55, 69
on froth, 197

Fagergren & Green machine, 458
Feed, regularity of, 648
to flotation, 212
Feeder, Stevens-Adamson, 637
Film flotation, 309, 482
contact, 285
removal of, 555
surface, 279
suspension, 1
Filming, quick, 343
Filter-presses, 563
Filtering, intermittent, 422
Flocculation, 365, 682
acids as affecting, 371
Flotation agents, coal-tar, 50
at Argo mill, 93
Flotation at Broken Hill Proprietary, 9, 21, 29, 196, 249, 273, 527, 545, 569, 654
at Butte, 25
at Central mill, 17, 580
at Chino, 505
at Cobalt, 509
at Cripple Creek, 79
at Dutch-App, 91
at Inspiration mine, 26
at Miami, 421, 436
at Mt. Morgan, 419, 436
at Pioche, 501
at Portland mill, 96
at Suan Concession, 148
at the Melones, 86
at the North Star, 81
by froth, 12, 654
cell, 410
Flotation, collective, 598, 667
concentrate, treatment of, 214
cost at North Star, 84
differential, 378, 396, 657
early work, 78
experiments, 33, 82
feed to, 212
film, 309, 482
froth in, 21
in Arizona, 530
in California, 402, 425, 429
in Chile, 429
in Colorado, 423
in Idaho, 427
in Mexico, 85, 536
in Montana, 428, 435, 437
in Nevada, 426
in Utah, 434
literature of, 670
mechanical developments in, 442
of bornite, 25
of chalcocite, 25
of galena ore, 569
of gold and silver, 78
of lead, 196
of oxidized lead ore, 30
of oxidized ores, 486, 669
of silver, 79
of silver ore, 509, 536

Flotation of slime-plant, 574
of tellurides, 79
of Utah Copper Co., 615
of zinc carbonate, 30
oils, 513
physics, 34
pneumatic, 153
poisons to, 347, 353
preferential, 605, 641
principles of, 248, 291
recoveries, 189
theory of, 267, 334
v. cyanidation, 86, 95, 193, 541
Flow-sheet for silver ore, 542
of Afterthought mill, 597
of Argo mill, 94
of Central mill, 571, 583
of Copper mill, 404
of slime-plant, 574
of tailing-plant, 576
Foams, stability of, 294
Free, E. E., 354
Freeman, C. C., 654
Froment, Alcide, 13, 14, 102
Froth affected by quartz, 327
disposal of, 161
experiments on, 197
flotation, 12, 654
in flotation, 21
making of, 74
nature of, 111, 288
quartz in, 327
Frothing-agent, 29, 649, 659
soluble, 349
process, discovery of, 205
Froths, 349, 680
Fry, Alfred T., 161

Gahl, Rudolf, 332, 506
Galena ore, flotation of, 569
Garfield smelter, 627
Gas, adsorption of, 677
condensation of, 280
Gold and silver, flotation of, 78
float and rusty, 79
Grease, natural, 273
Greenway, H. H., 382
Grinding, 208
Grinding, fine, 158, 185
of ore, 597
wet, 158
Groch impeller, 513, 515

Hague, William, 81
Hamilton, E. M., 98
Handy, R. S., 465
Hardinge mill, 413
Harvey, R. J., 569
Haynes, Wm., 4
Hazen, H. L., 610
Heating of concentrate, 411
Hebbard, James, 18, 196
Heller, A. H., 592
Henderson, Edwin T., 545, 559
Higgins, Arthur H., 17, 206, 454, 462
Higgins & Stenning machine, 452
Hildebrand, Joel H., 49, 53, 291
Historical, 3
Hoover, H. C., 12
Hoover, T. J., 11, 12, 24, 25, 28, 65, 133, 139, 252, 262, 660
Hoover machine, 145
Horwood, E. J., 379, 552
Horwood process, 257, 643
cost of, 608
in California, 592
modification of, 610
Hoveland, H. B., 488
Hyde, James M., 23, 100, 123, 150, 166, 469
Hyde machine, 470
Hydrogen sulphide, use of, 493
Hysteresis, 271

Idaho, flotation in, 427
Impeller, Groch, 513, 515
Inspiration mine, flotation at, 26
Intensifiers, 657
Interfacial tension, 335
conditions, 339

Jackling, D. C., 119
Janney, Frank G., 143, 615
Janney, T. A., 26
Janney machine, 141, 450, 540, 606, 618
Jones, Harry C., 260

K. & K. machine, 151, 448, 537
Kenrick, Frank B., 44
Kirby, Edmund B., 22
Krupp ball-mill, 208

Laboratory tests, 137, 166, 184
  work, 157, 170
Langmuir, Irving, 332
Launder machine, 472
Lavers, Henry, 381
Leaching, recovery of copper by, 586
  with brine, 519
Lead carbonate, treatment of, 492
  flotation of, 30, 196
Lewis, Robert S., 415
Lime, use of, 347, 538
  water, use of, 182
Literature of flotation, 670
Livingston, A. R., 483
Loring, W. J., 91
Lowden dryer, 635
Lyster, F. J., 383, 389

Machine, agitation, 174
  Callow, 153, 156
  Case, 147
  Elmore, 152
  Fagergren & Green, 458
  Higgins & Stenning, 452
  Hoover, 145
  Hyde, 470
  Janney, 141, 450, 540, 606, 618
  K. & K., 151, 448, 537
  launder, 472
  Owen, 155, 453
  pneumatic, 172, 175, 179
  Potter-Delprat, 140
  Roy & Titcomb, 149
  single-level, 665
  slide, 150
  standard M. S., 443, 664
  Wood, 139
Macquisten, A. P. S., 22
Magma Copper Co., 135
Magnesium sulphate, effect of, 186
Manganese compounds, 390
  ores, 399
Mathewson, E. P., 300
Mechanical developments in flotation, 442
Melones, flotation at the, 86
Meniscus, 337
Mexico, costs in, 191
  flotation in, 85, 536
Miami Copper Co., 27, 106, 113, 124
  flotation at, 421, 436
Mickle, Kenneth, 254, 678
Microscope, use of, 163
Middleton, Percy R., 586
Mill-tests, 189
Minerals Separation, 11, 12, 14, 23, 26, 115, 386, 395, 396, 521
Mishler, R. T., 182, 463
Molecular forces, 275, 300
Montana, flotation in, 428, 435, 437
Moulden, J. C., 201
Mount Morgan, flotation at, 419, 436
M. S. machine, 443, 664

Natural grease, 273
Nevada Consolidated, 134
Nevada, flotation in, 426
Nodulizing of concentrate, 638
Norris, Dudley H., 476
North Star, flotation at the, 81
  flotation costs at, 84
Nutter, E. H., 25, 393

Occlusion, 282
Oil, adhesion of, 59
  as a contaminant, 279
  buoyancy of, 1
  consumption of, 191
  critical point, 110, 112
  feeding device, 622
  films of, 67
  frothing, 123
  mixtures of, 95, 166, 185
  proportion of, 107, 206
  quantity used, 2
  viscosity of, 8
Oils, flotation, 513
  for flotation, 159
  selective action, 118, 287
  sulphuretted, 504
Oleic acid, 40

Oliver filter-plant, 625
Operating costs, 412, 520
Ore, flotation of oxidized, 486, 669
  grinding of, 597
  manganese, 399
  patents on oxidized, 486
  testing of, 137, 166
Osmosis, 263
Owen, T. M., 153, 390, 394, 461, 662
Owen machine, 155, 453
Oxidized copper ores, treatment of, 503
  lead ore, flotation of, 30
  ores, flotation of, 486, 669
  ores, patents on, 486
  zinc ore, 508

Pachuca tank, 125, 128, 155
Particles, classification of, 358
  electrification of, 254, 265
  size of, 198
  subsidence of, 363
Patents, 395
  Bacon, 379, 489, 491
  Bradford, 385, 387, 551, 553, 556
  Callow, 28
  Cattermole, 15, 103
  De Bavay, 10, 389
  Delprat, 10
  Dick, 486
  Elmore, 6, 21, 115
  Elmore vacuum, 118
  Everson, 3
  Froment, 13, 102
  Gahl, 506
  Greenway, 382
  Haynes, 4
  Hoover, 28
  Horwood, 379, 552
  Hoveland, 488, 490
  Kirby, 22
  Languth, 389
  Lavers, 381
  Lyster, 383, 389, 651
  M. S., 386, 390, 392, 395, 396
  Nutter, 393
  Owen, 390, 394, 662
  Potter, 10, 546
Patents, Ramage, 378
  Sulman, 5
  Sulman & Greenway, 107
  Sulman & Picard, 12, 17, 28, 101, 120, 487
  Terry, 488
  Wentworth, 378
Pearce, Jackson A., 93
Perkins, C. L., 334
Permanganate, alkaline, 391
Physical principles, 317
Pioche, flotation at, 501
Plant at the Central mine, 270
  cost of, 85, 194
  experimental, 203
Pneumatic equipment, 168
  flotation, 153
  machine, 172, 175, 179
Poisons to flotation, 347, 353
Portland mill, flotation at, 96
Potassium permanganate, 645
Potter, Charles Lee, 9
Potter-Delprat machine, 140
  process, 338
Preferential flotation, 605, 641
  methods, 663
Principles of flotation, 248, 291
  physical, 317
Pringle, L. B., 157
Process, Bradford, 559
  Cattermole, 199
  Delprat, 251
  Horwood, 257, 643
  Horwood, modification, 610
  Potter-Delprat, 338
Products, disposal of, 415
Pumps, centrifugal, 209
  scouring of, 209
Pyrite, effect of, 176

Quartz, froth affected by, 327
  in froth, 327
Quick filming, 343

Ralston, O. C., 248, 257, 283, 378, 442, 486, 672
Ramage, A. S., 378
Recovery of copper by leaching, 586

Recovery of silver, 183
Recoveries, flotation, 189
Reducing agent, acid as, 387
Re-grinding, 90
  cost of, 89
Residue, disposal of, 237
Rickard, T. A., 256, 259, 615, 626, 676, 681
Roasting, 397, 589
  fractional, 378
  of concentrate, 220, 432, 601, 633
Robbins, Hallet R., 402
Robson, George, 5
Rolker, C. M., 7
Rork, Charles E., 446
Rose, T. K., 332
Rowand, L. G., 485
Roy & Titcomb machine, 149
Royalties, 84, 97, 99

Sadtler, Samuel S., 54
Salts, use of, 346
Saponine, 65
Scouring of pumps, 209
Screen analyses, 577, 585
Separation-box, 562
Separatory funnels, 152
  vessels, 547
Shellshear, W., 12, 237, 578, 641, 666
Silica in concentrate, 430
Silver, flotation of, 78, 79
  ore, flotation of, 509, 536
  ore, flow-sheet for, 542
  recovery of, 183
Simpson, W. E., 509
Single-level machine, 665
Slide machine, 150
Slime, 357
  disposal of, 247
  plant, flow-sheet of, 574
  treatment of, 394, 551, 621
Smelting of concentrate, 431, 626
Smith, Ralph, 145
Smith, H. Hardy, 267, 524
Sodium sulphide, 496
Soluble frothing-agents, 349
Spitzkasten, use of, 198, 204
Standard M. S. machine, 443, 664
Stevens-Adamson feeder, 637
Suan Concession, flotation at, 148
Sub-aeration, 457
Subsidence of particles, 363
Sulman, H. L., 5, 49
Sulman & Picard, 15, 17, 20, 29, 101, 133, 381, 487
Sulphide filming, 496
Sulphides, alkaline, 390
Sulphur, colloidal, 77
  di-oxide, 77, 645
  volatilized, 567
Sulphuretted oils, 504
  hydrogen, 493
Surface films, 279
  tension, 33, 273, 277, 292, 311
  tension, measurement of, 42, 45
  tension, variable, 73
Surfaces, internal, 359
Suspensions, 299, 355
  coarse, 345
Suspensoids, 331

Taggart, A. F., 51, 63, 71, 673
Tailing, cyanidation of, 234
  distributing, 241
  plant, flow-sheet of, 576
Tellurides, flotation of, 79
Temperature, 185, 293
  critical, 303
Tension, 671
  interfacial, 335
Terry, Joseph, T., 488
Testing of ores, 137, 166
Tests, agitation, 170
  in bottle, 169
  in laboratory, 184
  in mill, 189
Theories, 655
Theory of flotation, 267, 334
Thickeners, Dorr, 237, 560, 565
Thornberry, M. H., 507
Tippett, J. M., 97
Towne, R. S., 28
Treatment of blende ore, 553
  of concentrate, 82
  of dump-slime, 572
  of flotation concentrate, 214

Treatment of lead carbonate, 492
of oxidized copper ores, 503
of slime, 394, 551, 621
Tube-milling, 182

Unloading of concentrate, 433, 631
Utah Copper Co., flotation of, 615
Utah, flotation in, 434

Vanner concentrate, 615
Viscosity, 61
Volatilized sulphur, 567

Wentworth, H. A., 378
Wetting, 46, 297, 314, 341, 646
Wood, Henry E., 10, 455
Wood machine, 139

Yerxa, R. B., 130

Zinc carbonate, flotation of, 30
concentrate, 212

DEC 20 1921

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541